Technical Report
2003 - 2004

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I. Introduction
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This report summarizes research progress during 2003-2004 for projects being conducted as part of the Global Climate and Energy Project (GCEP) at Stanford University. The current GCEP portfolio includes research in five areas:

1. Advanced combustion,
2. Renewable energy,
3. Hydrogen production, storage, and use
4. Advanced materials, and
5. Carbon capture and storage.

Each of these areas has potentially important roles to play in future systems that supply, transform, and use energy in a way that allows for substantially lower emissions of greenhouse gases than the systems in use today. Combustion, for example, is the primary means by which stored chemical energy in fossil fuels or biomass is made available for conversion into work. If more efficient means of conversion of chemical energy into work can be found, the emissions of CO₂, nitrogen oxides, and black carbon can be reduced. Renewable technologies, like wind and solar generation of electricity, for example, have the potential to reduce greenhouse emissions by offsetting the use of fossil fuels, if the costs of providing those technologies can be reduced so that they are competitive with other methods of generation. Molecular hydrogen is another form of stored chemical energy, one that must be manufactured using some other primary energy source. While oxidation of hydrogen for conversion of that chemical energy to work, in a transportation setting, for example, would not lead to carbon emissions, methods of hydrogen manufacture in common use today start with fossil fuels and do emit CO₂. Techniques that allow hydrogen production without CO₂ emission are needed if substantial use of hydrogen is to be accompanied by reductions in greenhouse gas emissions. Storage of hydrogen for use in transportation also involves significant challenges. The capture of CO₂ generated by combustion of fossil fuels or biomass or manufacture of hydrogen, along with subsequent storage of that CO₂ in a location other than the atmosphere may also contribute to reductions in carbon emissions. Research on advanced materials is connected to many of the other areas, including renewables, and hydrogen storage and use.

The chapters that follow describe research activities, report results, and outline future plans for projects being led by twenty-one principal investigators in ten departments at Stanford. Chapter II provides details for the following projects:

1. Hydrogen
   a. Biohydrogen Generation (Professors J. R. Swartz, Chemical Engineering and A. M. Spormann, Civil and Environmental Engineering) – develop an organism/bioreactor system employing a genetically engineered organism that will directly convert sunlight to hydrogen.
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b. Nanoscale Electrochemical Probes for Monitoring Bioconversion of Hydrogen (Professor F. B. Prinz, Mechanical Engineering) – develop nanoscale sensors to monitor the electro-chemistry of hydrogen production in microbes. The sensors are designed to measure reduction-oxidation reactions, electron transfer reactions, and the broader kinetics of biochemical processing within the cell.

c. Micro and Nano Scale Electrochemistry Applied to Fuel Cells (Professor F. B. Prinz, Mechanical Engineering) – delineate the relationship between electrocatalyst geometry and electrochemical behavior using platinum microelectrodes on a polymer electrolyte fuel cell. Develop the nanoscale technique of atomic force microscopy impedance imaging to allow highly localize measurements of electrochemical properties.


e. Hydrogen Effects on Climate, Stratospheric Ozone and Air Pollution (Professors M. Z. Jacobson, Civil and Environmental Engineering, D. M. Golden, Mechanical Engineering) – study the potential effects on global and regional climate, stratospheric ozone, and air pollution of replacing fossil-fuel-based vehicles and electric power plants with those powered by hydrogen fuel cells.

f. Solid-State NMR Studies of Oxide Ion Conducting Ceramics for Enhanced Fuel Cell Performance (Professors J. F. Stebbins, Geological and Environmental Sciences, F. B. Prinz, Mechanical Engineering) – develop new understanding of the atomic-scale structure and dynamics of the oxide ion conducting ceramic materials which are the heart of Solid Oxide Fuel Cells.

2. Renewable Energy

a. Nanostructured Photovoltaic Cells (Professor M. D. McGehee, Materials Science and Engineering) – develop efficient photovoltaic cells with semiconducting polymers that could be deposited in reel-to-reel coaters.

3. Carbon Capture and Storage

a. Assessing Seal Capacity of Exploited Oil and Gas Reservoirs, Aquifers and Coal Beds for Potential Use in CO₂ Sequestration (Professor M. D.
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Zoback, Geophysics) – develop tools to determine how changes in the state of stress in oil and gas reservoir rocks, coal beds, and aquifers with CO\textsubscript{2} injection affect the ability of those formations to retain the CO\textsubscript{2}.

b. Rapid Prediction of CO\textsubscript{2} Movement in Aquifers, Coal Beds, and Oil and Gas Reservoirs (Professors A. R. Kovscek and F. M. Orr, Jr., Petroleum Engineering) – develop efficient reservoir simulation tools to calculate how injected CO\textsubscript{2} will flow in oil and gas reservoirs, coalbeds, and saline aquifers.

c. Geophysical Monitoring of Geologic Sequestration (Professor J. M. Harris, Geophysics) – develop an appropriate suite of monitoring tools to detect movement of injected CO\textsubscript{2} in the subsurface.

4. Advanced Combustion


b. Development of Low-Irreversibility Engines (Professor C. F. Edwards, Mechanical Engineering) – investigate the potential to design and implement engines with significantly reduced irreversibility.

c. Sensors for Advanced Combustion Systems (Professor R. K. Hanson, Mechanical Engineering) – develop advanced sensors for use in energy systems that minimize environmental impact via control of combustion-generated pollutants such as NO, CO and unburned hydrocarbons, reduce CO\textsubscript{2} emissions by improving combustion efficiency and monitor the fugitive emissions from greenhouse gas sequestration efforts.


e. Process Informatics Model (Professor D. M. Golden, Mechanical Engineering) – convert the process of combustion chemistry model building into science, automate the methodology and make the information available in a prompt and convenient form on the Internet for researchers and designers of combustion equipment.

Chapter III reports progress in technical analysis activities that support the overall project. The first is a Systems Analysis project, led by A. J. Simon of the GCEP staff. This effort is intended to provide a capability for tracing of mass and energy flows for
energy systems, so that quantitative comparisons of energy technologies can be made, and to make that capability available for general use via web-based tools. The second is a project entitled Integrated Assessment of Energy Technologies, led by Professors John Weyant and James Sweeney in the Management Science and Engineering Department. The Integrated Assessment project is aimed at developing a comprehensive analysis system that can be used to estimate probable significance of technologies, to explore options to speed up diffusion of technologies, and to determine the magnitude of potential reductions in greenhouse gas emissions.

The current GCEP portfolio is only a beginning, of course. There are many additional areas that will need to be addressed in a balanced portfolio of research on energy technologies with low greenhouse gas emissions. Thus, the current research portfolio should be viewed as a work in progress, which will develop and grow as more projects are added in the next years.
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II.1 Introduction to Hydrogen Production, Distribution and Use

Hydrogen has been identified as a potential energy carrier in many low GHG energy scenarios. However, the technology to produce, distribute and use hydrogen in a cost-effective, low GHG manner is not yet developed.

Hydrogen can be produced from fossil fuels or from water splitting. When hydrogen is derived from hydrocarbons (fossil fuels), the chemical energy to be stored in the hydrogen is already present in the primary fuel. The key challenges to this form of production lie in controlling the chemical reactions and the extraction of hydrogen. Production from fossil fuels in a low GHG scenario will also require CO₂ capture and sequestration. Conversely, extraction of hydrogen from water requires that energy be supplied from an external resource, but does not present the challenge of unwanted emissions at the point of conversion.

Hydrogen's appeal as an energy carrier is limited by its ability to be efficiently stored. Many energy conversion systems that would use hydrogen must operate intermittently and thereby require a reservoir of hydrogen. This reservoir must be of reasonable size and weight, and cannot waste a significant fraction of stored energy in the filling and venting processes.

The two most likely candidates for the conversion of energy stored in hydrogen to useful work are internal combustion engines and fuel cells. Today's engine technology could be adapted for use with hydrogen at efficiencies comparable to hydrocarbon fueled engines, while advanced engine technology could push the boundaries of efficiency even further. Fuel cells hold the promise of higher efficiency than traditional engines, as well as other engineering tradeoffs that might make for quieter and possibly more reliable prime movers.

GCEP has six research efforts in the Hydrogen Technology Area. Production is addressed by Professors Swartz, Spormann and Prinz in their projects on biohydrogen generation and sensors for biohydrogen generation. The goal of these projects is to develop an engineering system based on a microorganism that can use the energy in sunlight to split water into hydrogen and oxygen. Professors Swartz and Spormann are developing the organism as an engineered hybrid between two naturally occurring organisms: one which harvests solar energy and stores it chemically, and the other which supplies stored chemical energy to the water splitting reaction. Professor Prinz is developing nanoscale probes to monitor this bioconversion process so that it can be further optimized.

Hydrogen storage on carbon nanostructures is addressed by Professors Cho, Clemens, Dai and Nilsson. The goal of this project is to develop a high surface-area, engineered nanocomposite material with the ability to adsorb and release hydrogen with very low irreversibility.
Professors Stebbins and Prinz are pursuing hydrogen usage in fuel cells in their projects on ceramic oxide ion conductors and micro and nano scale electrochemistry. These investigations will result in a better understanding of solid oxide and polymer electrolyte fuel cells which will aid in the creation of more efficient and robust designs.

Finally, Professors Jacobson and Golden have undertaken a study of the potential environmental effects of switching to a hydrogen economy. Replacing fossil-fuel based vehicles and electric power plants with those powered by hydrogen fuel cells may affect global and regional climate, stratospheric ozone, and air pollution.
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II.1.1 BioHydrogen Generation by Genetically Engineered Microorganisms
Part I: Engineering a Direct Pathway for Hydrogen Generation

Investigators
James Swartz, Professor, Chemical Engineering; Alfred M. Spormann, Associate Professor, Civil and Environmental Engineering, Biological Sciences, and Geological and Environmental Sciences; Chia-Wei Wang, Postdoctoral Researcher, Chemical Engineering; and Marcus Boyer and Keith Gneshin, Ph.D. Candidate Graduate Researchers, Chemical Engineering

Introduction
The longterm goal for this project is to develop efficient and economical technology for the biological conversion of solar energy into molecular hydrogen. The first portion of the project (Part I) seeks to develop an organism/bioreactor system employing a genetically engineered organism that is effective in the DIRECT conversion of sunlight to hydrogen. The organism will use a shuttle protein, ferredoxin, to transfer electrons from the reaction of water photolysis to the hydrogenase enzyme.

The following diagram (Figure 1) shows that this pathway is simple and short and therefore offers attractive conversion efficiencies. The photosystem of a bacterium such as *Synechocystis* captures sunlight and splits water to generate molecular oxygen, protons, and mobilized electrons. These electrons are transferred to an electron carrying protein, ferredoxin. We propose to introduce into the cyanobacterium a new hydrogenase enzyme that will accept the electrons from ferredoxin and combine them with the protons to make molecular hydrogen. However, the first and major problem is that existing hydrogenase enzymes are inactivated by molecular oxygen. Thus, the initial focus is to evolve a highly active hydrogenase to be resistant to inactivation by molecular oxygen.

Solar Energy

![Diagram of proposed *Synechocystis* bacterium engineered to support a short, efficient pathway for the conversion of sunlight and water into molecular hydrogen. As shown, the dominant barrier to this technology is the availability of an oxygen-tolerant hydrogenase enzyme.]

BUT, O₂ Inactivates Known Hydrogenases

Figure 1: Diagram of proposed *Synechocystis* bacterium engineered to support a short, efficient pathway for the conversion of sunlight and water into molecular hydrogen. As shown, the dominant barrier to this technology is the availability of an oxygen-tolerant hydrogenase enzyme.
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Background

A recent Sandia Labs study suggests that the sunlight incident on a 100 square mile area in southern Nevada could supply all of the U.S. energy needs. This is equivalent to only 1.7% of the current U.S. cropland area! However, we need an efficient and cost effective method to convert that sunlight into useable energy. Ideally, a significant fraction would be converted into a clean, portable fuel such as hydrogen.

Therefore, we are committed to the development of an efficient biological process to produce hydrogen from sunlight and water. The power of modern genetic engineering techniques, the proven success of protein evolution technologies, and the extensive knowledge of photosynthesis and bacterial metabolism combine to suggest the feasibility of our proposed project. The proposed reaction system is envisioned approximately as shown in Figure 2.

Figure 2: Diagram of a proposed production system for hydrogen production.

The heart of the system is a very large surface area collector/reactor designed to collect the sunlight, remove the evolved gases (H₂ and O₂), control system temperature, and provide optimal mixing patterns. Initial calculations suggest a relatively thin bioreaction layer (less than 1 cm.) is required for the culture to completely absorb available energy. This culture would continually flow through the reactor using a static mixing design to quickly cycle individual organisms between bright and dark conditions (at the top and bottom of the culture channel). The cyclic light exposure will be designed to avoid damage to the light adsorption complexes in the microorganisms caused by constant exposure to bright sunlight. The top of the bioreaction channel would be bounded by a transparent gas permeable membrane. This membrane would allow the evolved H₂ and O₂ to be removed into an upper channel (maintained under vacuum) to maintain low H₂ and O₂ partial pressures in the bioreaction channel. A bottom channel below the reaction channel will carry the temperature control fluid.

As exciting as this prospect is, it is totally dependent upon the availability of a new hydrogenase enzyme that remains active in the presence of the oxygen. Developing such an enzyme is now our primary objective for Part I. WE ARE NOT AWARE OF ANY OTHER SERIOUS EFFORTS TOWARD THIS OBJECTIVE. Because the 3-D structure of the Fe-S hydrogenase (CpI), from Clostridium pasteurianum was known (Ref. 1), because it couples to ferredoxin with high turnover numbers, and because it is an
iron-sulfur hydrogenase with a somewhat simpler active site structure than for Ni-Fe hydrogenases, we chose that enzyme as our first target for evolution to oxygen tolerance.

Current technology does not allow us to \textit{a priori} select the amino acid changes that would provide the oxygen tolerance. Instead, it is now a well-established strategy to pursue a protocol called “protein evolution”. We first must generate genetic diversity within the initial DNA sequence that encodes for expression of the protein. This part is generally straightforward. The more difficult challenge is establishing methods for searching through 10’s of thousands of candidate proteins to find the few that have the new property of oxygen tolerance. If we can develop this capability, we can then iteratively search for enzymes with better and better oxygen tolerance. Fortunately, we believe that our laboratories have a unique set of skills that, when combined, will allow us to conduct this search relatively quickly and effectively.

For the protein evolution to proceed quickly and effectively, we will capitalize on the many advantages offered by cell-free protein synthesis technology. Using this approach, we potentially can synthesize a number of hydrogenase candidates in each well of 96-well microtiter plates. We can also establish procedures that will let us process many 10’s of plates per day. Each candidate protein will have an extension that will absorb onto the wall of the microtiter plate well. When the reaction is completed, the well will be washed clean of the reaction solution, but the product hydrogenase will be retained. Then, we can assess the activity of the hydrogenase by taking advantage of the nature of the hydrogen producing reaction:

$$2 \text{ Reduced Ferredoxin} + 2 \text{ H}^+ \rightarrow 2 \text{ Oxidized Ferredoxin} + \text{H}_2$$

If the hydrogenase retains its activity in a controlled oxygen environment, hydrogen production activity will be driven by the reduced ferredoxin, protons will be consumed, and the pH will rise. The pH rise can easily be detected using a colored pH indicator dye. To ensure that we are conducting the authentic reaction desired for the photosynthetic \textit{Synechocystis} strain, we will use the \textit{Synechocystis} ferredoxin (in the reduced form) to supply the electrons required for hydrogen generation. Thus, to implement our search, we must establish the following capabilities:

1. Production, purification, and reduction of \textit{Synechocystis} ferredoxin,
2. Ability to generate diversity in the hydrogenase gene and to conveniently and reliably provide DNA templates for cell-free synthesis in 96-well plates,
3. Ability to express active hydrogenase enzyme in the cell-free system,
4. Ability to purify (retain) the expressed hydrogenase in the microtiter plate well,
5. Ability to sensitively detect activity and increased oxygen tolerance, and
6. Ability to recover the DNA that encodes for the improved hydrogenase.

As reported last year, we quickly accomplished objective number one. Objective number two proved to be significantly more difficult than most people would expect. It requires reliable DNA replication using the polymerase chain reaction to produce $10^{12}$ identical DNA molecules from a single molecule of DNA. Furthermore, this amplification must be achieved with identical yields for every mutated gene. This is truly “pushing the envelope” in terms of DNA replication technology. However, Keith
Gneshin has made excellent progress and is nearly complete in providing the technology we need (see Results; Part A).

Objective three, the expression of active hydrogenase has proven to be very difficult. Chia-Wei Wang has identified conditions that provide a hint of activity, but not enough for an evolution program. These efforts are summarized in the section entitled: Results, Part B. The lack of success motivated a project by Marcus Boyer to investigate the cell-free synthesis of the *Synechocystis* ferredoxin, a smaller and simpler Fe-S protein. This effort has been very successful as detailed in Results: Part C. The ferredoxin success suggests the feasibility for producing more complex Fe-S proteins, but also suggests that we should broaden our search to investigate the folding of other hydrogenases that are somewhat simpler in structure than the Clostridial enzyme. Objective four was also investigated by Chia-Wei Wang to suggest that the affinity afforded by the commonly used his₆ purification tag with metal chelation adsorption is probably not sufficient (also discussed in Results: Part B). Systems with higher affinity will now be evaluated. The last two objectives have not been addressed as yet but are not expected to be difficult. Our goal now is to demonstrate successful hydrogenase evolution and initial hydrogen generation by *Synechocystis* by the end of next year.

**Results: A) Reliable PCR Amplification of single DNA molecules (Keith Gneshin)**

**Objectives:** The success of the hydrogenase evolution project depends, in part, on our ability to fairly evaluate each candidate mutant. To accomplish this, we have carefully focused on the initial stage of the screen which is intended to utilize the polymerase chain reaction (PCR) to amplify every individual molecule of DNA into upwards of one trillion copies of the original template.

Our objectives in this work have been:

1) to ensure that every mutant DNA template introduced into the screen is fully amplified,
2) to ensure that every mutant DNA template is amplified equally relative to other templates in the screen and
3) to devise a complete protocol that ensures reproducible amplification.

The first objective requires a PCR protocol that minimizes the random loss of library members. While some template degradation is inevitable prior to and during PCR, we want to maximize the probability that we can evaluate each and every mutated DNA sequence. Our second objective is to create a PCR protocol that minimizes amplification bias between various members of our library both within a screening well and between separate wells. A final objective is to develop DNA handling protocols, including such tasks as sample transfer, DNA purification, and DNA storage, which ensure reproducible results when the actual PCR is performed. We believe these objectives, when realized, will maximize our ability to identify the very rare but very important mutations that will improve enzyme performance.
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Understanding the importance of these three objectives requires a consideration of the intended goal of the hydrogenase screen. Our stated goal of developing an oxygen-tolerant hydrogenase enzyme will require exploring a large number of mutant proteins to find the most beneficial combination of individual mutations. The expected method for generating this library of hydrogenase mutants is family gene shuffling, a recombinant PCR method that allows multiple related genes to be combined in a manner that mimics \emph{in vivo} gene recombination. The biggest benefit of family gene shuffling is that it pools together the mutations within a single gene that have already been selected as beneficial by the source organisms. In this respect, the variants explored are more likely to contain complementary mutations rather than deleterious random ones. When compared to methods of random gene mutation such as error-prone PCR, the speed at which desired proteins are isolated from a gene library is much faster via gene shuffling.

A gene sequence that leads to an oxygen-tolerant hydrogenase is expected to be very rare. Because of this, we are developing a high-throughput screening method that allows us to very specifically isolate a member of a gene mutation library and test the activity of the resultant enzyme. A basic diagram of our proposed screening method is shown in Figure 3. Following the generation of our hydrogenase library by family shuffling, mutants will be diluted to a very low concentration then dispensed into individual screening wells with a single DNA encoding each of approximately five to ten mutants per well. Once the library has been divided up, PCR reagents can be added to each well. From the initial DNA templates, each mutant will be amplified by a factor of $10^{12}$. These PCR products will serve as templates for coupled transcription and translation by the cell-free protein

![Figure 3: Approach to high-throughput screening using PCR and cell-free protein synthesis in multi-well microtiter plates.](image-url)
synthesis technique employed in our laboratory. Our current work in developing the previously described screening method centers on the polymerase chain reaction. We believe this aspect of the screen warrants the most attention because the ability of cell-free protein synthesis to occur is entirely dependent upon having adequate amounts of DNA template to transcribe and translate into protein.

Cell-free protein synthesis and enzymatic activity assays are methods that have been developed and employed in our laboratory. However PCR driven DNA amplification from very low DNA concentrations is a sensitive task that has required significant and careful study. As detailed below, initial work showed that routine PCR approaches failed miserably in this much more demanding task.

**Initial Problems with PCR Protocol Have Been Resolved.** The development of a PCR protocol for our high throughput screen has been a difficult problem that has led to some surprising findings. Although this aspect of our work has taken longer than anticipated, we are very close to having a reproducible procedure in place for amplifying single molecules of DNA as required in our screening scheme. While PCR has been a ubiquitous technique in biochemistry for nearly 20 years, our screen demands much more of the PCR reaction than is typically required. Most PCR reactions are performed at high starting template concentrations, requiring only up to one million-fold amplification of the target sequence. The hydrogenase screen will require an additional six orders of magnitude of amplification. This additional amplification more than doubles the length of the reaction. At such long time scales, the stability of PCR reagents is tested and minor perturbations for a typical reaction will cause the failure of the longer, more demanding amplification. These difficulties have posed challenges to our development of the high-throughput screen. For example, we have encountered: a) the thermal degradation of linear DNA templates leading to low yields or reaction failure, and b) a large variety of aberrant reaction products caused by poor primer characteristics, poor purification reagents, and metal contamination. We have already found technical solutions to all of these problems and believe we only need to develop an effective template dilution method to complete this work.

Prior to attempting single-molecule PCR, we wanted to demonstrate an effective protocol for amplifying high concentrations of initial DNA template, with upwards of ten million starting copies. While this is a fairly common initial concentration for PCR, we encountered initial difficulty because our starting templates were linear DNA rather than circular plasmid DNA. A literature search revealed a mechanism for thermal degradation that severely affected linear DNA templates. The solution to this problem was to drastically reduce the duration of the high temperature steps in the PCR protocol. Successive PCR reactions showed highly-reproducible amplification for a wide range of initial template concentrations.

Ensuing work focused largely on locating an effective primer for single-molecule PCR. We initially used a unique primer to amplify each strand of the double-stranded DNA template (in this case, the sHydA gene encoding for the clostridial hydrogenase). These primers worked well for the original gene sequence, but the primers tended to
produce improper, shortened products for mutated versions of the gene, as shown in Figure 4A. Each lane shows the reaction products for the hydrogenase gene with the same restriction site sequence located in a different place in the gene. The lower bands represent undesired side products. The improper products were attributed to mispriming of the template sequence. We solved this problem by converting to a single-primer format. By using only a single primer to initiate replication for both DNA strands and optimizing its sequence, we were able to develop a primer that had minimal complementarity to the gene sequence outside of the intended priming sites, minimizing the chances of mispriming. This technique also had the advantage of allowing us to choose a primer with a favorable high annealing temperature and minimal self-complementarity, reducing the chances of primer-dimer formation which can also lead to aberrant PCR products. Single-primer PCR was far more reliable than the original double-primer PCR for amplifying a series of unique mutants of our hydrogenase gene, as shown in Figure 4B.

![Image of PCR products](image)

**Figure 4:** A) Aberrant products developed from hydrogenase mutant genes during double-primer PCR B) Elimination of aberrant products by single-primer PCR.

We also found DNA purification to be problematic during the course of our early PCR work. To demonstrate the reproducibility of a PCR protocol, we needed to transfer the products from an initial reaction into a successive set of PCR reactions. Before the actual DNA transfer to the new reactions, we would attempt to purify the DNA products to remove any deleterious carryover from the previous reactions. Results in the second PCR were initially variable; the source of the problem was ultimately traced to our purification protocol. At the time, spin columns were used to trap DNA while other PCR reactants were washed away. It was found that spin columns tended to completely fail at the rate of 1 in 6 attempts, even when purifications were carried out in parallel with identical reagents, as shown in Figure 5. We never successfully determined what aspect of this purification technique was failing. We avoided the problem by adopting the more labor-intensive but more effective technique of phenol-chloroform extraction of DNA. With this purification method, we were able to carry DNA through a series of reactions without failures. While this purification problem was ancillary to the actual PCR protocol, it nonetheless represents a major factor in ensuring successful amplification of DNA.
II.1 Project Results: Hydrogen

Figure 5: Spin column purification failure. Six PCR reactions were conducted in parallel and purified. The reaction run in lane 4 was successful but the purification failed completely.

A final major problem that we have encountered is metal contamination. This problem has only become apparent now that we have begun to actually attempt amplification from a single molecule of DNA. At very low template concentrations, we saw only two results: successful amplification of our hydrogenase template or an undesired short product. An example of these results is shown in Figure 6. At no point did we see these two products occurring simultaneously within a single reaction,

Figure 6: Primer-dimer accumulation in single-molecule PCR. Left lanes are reactions performed from an approximate starting concentration of 10 molecules of template per reaction. Right lanes began with approximately 1 molecule per reaction.

suggestions that they were in competition with each other for available primers during the early stages of the amplification. An initial speculation was that a trace metal contamination could have caused our primers to associate with each other just enough to cause a primer dimer to form. Control reactions without any DNA template showed none of the aberrant product (see Figure 7). We suspected that the potential source of metal contamination was the DNA template itself. To test this hypothesis we added EDTA, a metal-chelating agent, to our DNA before adding it into the PCR reaction. The result was a complete elimination of the aberrant product, shown in Figure 7. Under typical conditions, the EDTA is capable of suppressing primer dimer formation to allow reliable
amplification of our hydrogenase gene. The very light product band in lanes 6-10 suggests that further work is needed for reliable amplification from single DNA molecules, but clearly the primer dimer threat has been dramatically reduced.

**Figure 7:** Elimination of primer-dimer accumulation with EDTA. Lanes 1-10 contain 1.0 \(\mu\)M EDTA. Lanes 1-5 have 100 templates per reaction initially, and lanes 6-10 have 10 templates. Lanes 11-20 contain no EDTA. Lanes 11-15 have 100 templates initially and lanes 16-20 have 10 templates. Lanes 21-25 are no-template controls with 1.0 \(\mu\)M EDTA.

With these problems solved, we have made significant progress toward satisfying our DNA amplification objectives. To create a robust PCR technique that minimizes random loss due to thermal degradation, we have chosen an unconventional PCR cycling pattern that greatly minimizes the length of time our template is exposed to high temperatures. Also, in an effort to minimize misannealing, we’ve chosen a primer that anneals at the extension temperature of the polymerase enzyme thereby eliminating the need for the low-temperature annealing step in the typical PCR cycle. Figure 8 shows the changes we have made to the standard PCR protocol. Despite these significant changes to the PCR protocol, we still get efficient and reproducible amplification of our gene target.

We have also shown that single-primer PCR can amplify mutant genes in a library without significant bias toward any particular members. To do this, we created a series of mutants of our sHydA (synthetic Clostridial hydrogenase) gene, each having a different location for the recognition sequence for a restriction enzyme. Each member of the mutant library was added in equal concentration to a PCR reaction and then amplified simultaneously. Following the PCR, the product was digested by the appropriate restriction enzyme, causing each mutant to be cut at its unique recognition site. The result was a range of DNA fragments, each of which could be attributed to a particular mutant from the library. Qualitatively, all members of the mutant library were seen in the final digestion product, meaning all were amplified to roughly the same extent as seen in Figure 9. While the qualitative result suggests we can perform PCR without bias toward particular members, we intend to perform a more rigorous quantitative experiment to verify this result.
II.1 Project Results: Hydrogen

Figure 8: Revision to standard PCR protocol for single-molecule PCR. Times are given in minutes. Boxed regions represent the actual cycling pattern of the PCR, repeated up to 65 times.

Figure 9: Equality of amplification among coamplified hydrogenase mutants. The brightest band is the actual hydrogenase gene and the shorter bands are fragments from digested genes.
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Finally, we are almost to the point of being able to amplify a single-molecule of DNA to a very high concentration. Our recent attempts showed acceptable amplification with approximately 100 molecules of initial template (Figure 7). However, further dilution has produced variable results. We believe that most dilution problems have thus far been tied to metal contamination issues. Now that we know how to mitigate this problem, we believe we will be able to more successfully dilute DNA down to the single molecule level and amplify from there.

Summary and Future Work (Results: Part A). We have developed a robust method for amplifying DNA targets from low concentrations of starting template. In order to do so, we have adopted a unique protocol for our PCR reactions. The abbreviated PCR cycle profile was chosen to increase the success of the PCR procedure, but it has also produced a practical benefit. Our original PCR method would have required nearly six hours to complete when amplifying from the single molecule level. Our current abbreviated protocol requires just over three hours. This time savings now makes it feasible to conduct the entire protein screen, from DNA amplification through activity assay, within a single day. Making each round of screening a one-day process will accelerate our hydrogen evolution project.

Our last remaining issue before we complete this work is perfecting our template dilution method. Once we can reproducibly produce single molecule template concentrations in our PCR reactions, we believe we will have all of the technique in place for the PCR portion of our screen. We will be performing several quantitative experiments soon to verify our results, and we believe this portion of the project will be completed by July 2004. The in-place activity assay is expected to be straightforward. Thus, the remaining obstacle is the cell-free expression of active hydrogenase as discussed in the next section.

Results: B) Expressing Active Hydrogenase in a Cell-Free System.

This is by far the most significant challenge for the project at this point and therefore has received the most attention. The hydA gene encoding the Clostridial hydrogenase was cloned into expression plasmids for both in vivo and cell-free expression. It was found that the protein could be expressed with a his6 (His) purification affinity tag either at the N-terminus or the C-terminus of the protein. Evaluation to date has indicated moderate expression of the hydrogenase polypeptide in the cell-free system with the extracts from \textit{E. coli} and \textit{Clostridium pasteurianum}, and a tiny amount of activity seems to originate from the newly synthesized HydA with a His tag compared to the control.

As reported last year, initial expression with the native hydrogenase gene suggested a problem with rare codons (codons rarely used by \textit{E. coli}). Therefore, we designed and synthesized a completely new gene sHydA containing the preferred codons for \textit{E. coli} using primer overlap PCR extension reactions. The use of the new gene approximately doubled protein yields but produced no active hydrogenase with only \textit{E. coli} S30 extract even when carbamoyl phosphate, ferric ammonium sulfate, and sodium sulfide were
added as sources of the chemical entities required to assemble and localize the iron sulfur centers. To assist in hydrogenase folding, we added a cell extract from the Clostridial strain that naturally makes the hydrogenase in the hope that important helper proteins will be provided. The challenge with this approach is that the Clostridial extract also carries a strong background of hydrogenase activity. This makes it difficult to determine if new activity has been formed in the cell-free reaction. To overcome this, we used the clone of HydA with a his\textsubscript{6} tag as our target protein for cell-free synthesis. After the cell-free reactions with the radio-labeled \[^{14}C\]leucine, we can quantify the yields of the newly synthesized proteins by measuring the incorporated radioactivity and can remove the background hydrogenase activity by using the his\textsubscript{6} tag to retain the newly synthesized hydrogenase in metal chelation adsorption wells while washing away the other reaction components. We used the clone of HydA with the N-terminal his\textsubscript{6} tag in most experiments since the tag is assumed to be more accessible for purification based on the crystal structure of the enzyme.

In all cases, the standardized \textit{E. coli} S30 cell extract was used and the Clostridial extracts were added in different portions as indicated (Fig. 10). The total protein yields were measured, and the cell-free reaction mixtures were also centrifuged to obtain the soluble fractions for protein quantification. We found that the addition of the Clostridial extracts reduced the yields of the proteins synthesized from the cell-free reactions for both the control protein chloramphenicol acetyl transferase (CAT) and for our target protein, HydA. It is interesting to notice that this inhibitory effect from the addition of the Clostridial extract is even more severe for CAT than for HydA.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure10.png}
\caption{In vitro expression of hydrogenase. CAT is used as an expression comparison; CAT-CHis is the CAT protein with a C-terminal his\textsubscript{6} extension. HydA represents the \textit{Clostridium pasteurianum} hydrogenase encoded by the synthetic gene sHydA; NHis-HydA is the same protein with an N-terminal his\textsubscript{6} extension. The volume ratios between \textit{E. coli} and Clostridial extracts in the cell-free system are listed, e.g. 3:1 represents that 3 volumes of \textit{E. coli} extracts were used plus additional 1 volume of Clostridial extract.}
\end{figure}
Since adequate protein synthesis was obtained in all cases, we proceeded to purify and assay the synthesized his6-tagged enzymes using commercially available Ni-chelation microtiter plates. The typical procedure includes loading the soluble fractions from the cell-free reaction mixtures into the wells of the plates, incubating to allow the his-tagged proteins to absorb to the walls of the microtiter plate wells, and washing to remove the background proteins. Finally, we can elute out the bound proteins from the wells for protein assays or can add assay reagents directly into the wells to determine enzymatic activity. We added colorless, oxidized methyl viologen into the wells and monitored the formation of the blue color associated with the product of the hydrogenase reaction, reduced methyl viologen. Typical results are presented in Table I. They indicated that the his6 tag is not effective in retaining low concentrations of soluble product in the wells. However, the results also suggest the formation of hydrogenase activity associated with HydA expression. This is encouraging data, but the activity is much less than would be expected from this quantity of adsorbed hydrogenase if it were fully active. These results are therefore prompting us to examine the expression of alternative, somewhat simpler hydrogenases from blue-green algae.

Table I: Retention in the Ni-chelation microtiter plate wells and hydrogenase activity of the His6-tagged reaction products produced as in Figure 10. The absorbed protein was eluted from the wells using 250 mM imidazole and the yields were measured by radioactivity. The reduced methyl viologen signal was measured at 560 nm (OD560) after overnight incubation to assess hydrogenase activity.

<table>
<thead>
<tr>
<th>Extract Mix, E. coli : Clostridial</th>
<th>Protein of Cell-free Synthesis</th>
<th>3:0</th>
<th>3:1</th>
<th>3:2</th>
<th>3:3 (1:1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eluted Protein (ng)</td>
<td>CAT</td>
<td>HydA</td>
<td>CAT</td>
<td>HydA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>39.68</td>
<td>20.73</td>
<td>20.77</td>
<td>5.16</td>
</tr>
<tr>
<td></td>
<td>Methyl Viologen Signal (OD560)</td>
<td>0.02</td>
<td>0.10</td>
<td>0.11</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Retention of His-tagged Product in the Microtiter Plate Wells. The plates we used for purifying the His-tagged proteins were coated with nickel (Ni-NTA) and the dissociation constant Kd of His6 to Ni-NTA is on the magnitude of 10^-6 M. In contrast, typical antibody binding affinities have Kd values ranging from 10^-7 M to 10^-10 M or lower. Thus, we will evaluate the use of anti-his tag antibodies for product adsorption. For example, the Tetra-His antibody has a dissociation constant, Kd, of 10^-8 to 5*10^-8, and the Penta-His antibody has a Kd of 5*10^-8 to 10^-9. We are now evaluating the Penta-His antibody.

Developing Antibodies for Removal and Purification of the Native Hydrogenase. In addition to the efforts for the expression of active hydrogenase in a cell-free system, we pursued the development of an affinity purification reagent that will allow us to remove the major hydrogenase enzyme from the Clostridial extract. This same reagent should allow us to purify native hydrogenase to use as a comparison standard. We used the technique of phage display to identify monoclonal antibodies suitable as the affinity purification reagents. First, the sHydA gene with the N-terminal
His-tag was expressed *in vivo* in *E. coli* to prepare large quantities of NHis-HydA proteins. Although not active, the soluble HydA polypeptide can serve as the antigen for antibody screening procedures. The soluble fractions of the expressed HydA protein with the His-tag were purified at a larger scale using the Ni-chelation columns of the His-Trap Kit (Amersham Biosciences, now part of GE Healthcare, Piscataway, NJ).

After dialysis with the PBS buffer, the purified NHis-tagged HydA in PBS was used as the antigen in coating immunotubes. We grew the Tomlinson libraries I & J (MRC Centre for Protein Engineering, UK) and selected bacteriophage against the antigen through three rounds of selection. Phage were screened for binding by polyclonal and monoclonal ELISA to isolate antibody candidates. Finally, we produced soluble monoclonal ScFv antibody fragments in *E. coli* strain HB2151 and purified them using Ni-NTA spin columns. From these phage display procedures, we identified five distinct soluble monoclonal antibodies with diverse CDR (complementarity determining region) sequences of the VH (variable heavy) chain of the antibody. All five can potentially serve as affinity purification reagents.

**Summary and Future Work (Results: Part B).** We now achieve reliable expression of his6 tagged Clostridial hydrogenase polypeptides. Conventional metal chelation microtiter plates do not appear to provide sufficiently high adsorption affinity to completely capture the expressed protein. Antibody adsorption will now be tested. Although small amounts of hydrogenase activity have been produced after mixing Clostridial cell extracts into the reaction mixture, the activity levels reflect a very small fraction of the expressed protein. Additional changes in the expression and folding environment will be tested, but it may be that this hydrogenase is too difficult to assemble for present cell-free protocols to be successful. As described below, additional hydrogenases will now be evaluated in parallel to this effort.

**Results: C) Cell-free Production of Active Ferredoxin**

**Executive Summary: Cell-free Production of Ferredoxin**
- Hydrogenase is a complex protein that incorporates clusters of inorganic iron and sulfur that make protein maturation a challenge in a cell-free environment.
- To better understand conditions favorable to iron-sulfur cluster formation, we have expressed a simpler model iron-sulfur protein called ferredoxin from the cyanobacterium *Synechocystis* sp PCC 6803.
- Upon supplementation of iron and sulfur sources, the cell-free system can efficiently express and mature ferredoxin to a fully active form.
- Increasing the concentration of iron-sulfur cluster helper proteins changed the optimal supplementation levels for the iron and sulfur source molecules, but did not increase the overall yield of active ferredoxin.
- When compared with ferredoxin produced in *E. coli*, cell-free ferredoxin is equally active.
- The understanding gained from expression of ferredoxin is being applied toward expression of the more complicated hydrogenase enzyme.
Ferredoxin as a model iron-sulfur protein. Hydrogenase belongs to the family of iron-sulfur (Fe-S) proteins distinguished by their incorporation of inorganic iron-sulfur clusters. These clusters compose the active sites of the proteins and are necessary for their electron transfer activity. Installation of iron-sulfur clusters requires reduced iron and sulfur sources as well as other helper proteins. The expression and maturation of an iron-sulfur protein has not previously been accomplished in any reported cell-free system.

Anticipating the challenge of maturing the complicated Fe-S protein hydrogenase in the cell-free system, we began in parallel the expression and maturation of a simpler Fe-S protein, ferredoxin from the cyanobacterium Synechocystis sp PCC 6803, the organism intended for use in biohydrogen production. By successfully expressing and maturing ferredoxin, we have learned about conditions favorable for Fe-S cluster formation in the cell-free system.

Ferredoxin is a small protein, is highly acidic, and contains one 2Fe-2S cluster. Its homologues serve as electron carriers in many organisms and as electron donors to Fe-type hydrogenases. Synechocystis ferredoxin was found to be highly soluble, and easily purified. An activity assay was developed to measure the activity of ferredoxins synthesized in our lab. For these reasons, ferredoxin has served as an ideal model Fe-S protein for the cell-free system.

No quantitative assay for ferredoxin activity was found in the literature. Therefore, an assay was developed using the following reactions:

\[
\text{NADPH} + \text{Fd}_{\text{ox}} \rightarrow \text{Fd}_{\text{red}} + \text{NADP}^+ \\
\text{Fd}_{\text{red}} + \text{CytC}_{\text{ox}} \rightarrow \text{Fd}_{\text{ox}} + \text{CytC}_{\text{red}} \text{ (colored)}
\]

Enzyme and substrate concentrations were adjusted until the rate of CytC reduction was dependent upon the concentration of redox active ferredoxin. This proved to be a useful and highly repeatable method for determining the concentration of competent ferredoxin.

Iron and Cysteine Supplementation. To supply the iron and sulfur for formation of the Fe-S cluster of ferredoxin, we supplement the cell-free reaction with ferrous ammonium sulfate and with the amino acid cysteine. Some Fe-S proteins have been refolded in vitro using an inorganic sulfur source (Ref 2), but natural systems provide sulfur by the enzymatic desulfuration of cysteine (Ref 3). Figure 11 shows the effect of supplementation of iron and cysteine on the cell-free production of ferredoxin. Addition of iron to a reaction containing the standard level of cysteine provided for protein synthesis had only a small effect on protein production and activity. Addition of cysteine beyond the standard amount without any addition of iron is beneficial for protein production, but has no effect on activity. Supplementation of both iron and cysteine causes a significant increase in both protein production and activity indicating that the effects of these factors are coupled.
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Figure 11: Supplementation of Fe and Cysteine has a synergistic effect on ferredoxin protein production and activity

ISC Helper Proteins. In addition to the presence of iron and sulfur sources, helper proteins are required to assemble and install some iron-sulfur clusters. Nakamura, et. al. have shown that the coexpression of the 9-protein *E. coli* ISC operon improves yields of ferredoxins produced *in vivo* (Ref 4.) To test whether increasing the concentrations of these proteins would have an effect on the cell-free system, we obtained the plasmid containing the *E. coli* ISC operon. This plasmid was transformed into a cell extract source strain of *E. coli*. Expression was induced during the growth of the extract source cells to increase the abundance of these proteins in the cell-free extract. This extract is referred to as pRKISC extract after the name of the plasmid containing the ISC proteins.

Use of this extract slightly decreased the optimal levels of Fe and cysteine supplementation (Figure 12). However, the total yield and specific activity of ferredoxin produced by this extract were not improved. It would appear that an overrepresentation of ISC helper proteins results in the more efficient use of iron and cysteine, but the same expression and maturation results can be obtained from standard extract by increasing supplemented iron and cysteine concentrations.

Characterization of Purified Ferredoxin. Ferredoxin was produced *in vivo* by overexpression in *E. coli*. This ferredoxin was purified and used as a reference against which to compare the ferredoxin produced in the cell-free system. Ferredoxin was also purified after cell-free synthesis using either the lab standard extract (KC1 Fd) or the extract with overexpression of ISC proteins (pRKISC Fd). The activity, iron content, and protein concentration of purified samples was measured. The activity of both cell-free ferredoxin samples was found to be at least equal to the activity of ferredoxin produced in vivo on a per-iron basis (Figure 13). The amount of iron incorporated per protein in each sample was also very similar. In short, cell-free expression of ferredoxin produces fully active ferredoxin with approximately the same maturation efficiency as recombinant *in vivo* expression in *E. coli*. 
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**Peak Specific Activity of Cell-free Ferredoxins**

![Bar chart showing specific activity of ferredoxins.]

**Peak Protein Production of Cell-free Ferredoxin**

![Bar chart showing protein production of ferredoxins.]

**Figure 12:** Specific activity and protein production of ferredoxin produced in the cell free system under conditions optimized for lab standard extract (KC1) or extract enriched for ISC helper proteins (pRKISC).

**Activity of Ferredoxins on Per-iron Basis**

![Bar chart showing activity of ferredoxins.]

**Figure 13:** Purified cell-free ferredoxin is as active as ferredoxin produced in *E. coli*.
UV-Vis Absorbance Spectrum of Purified Cell-free Ferredoxin. The UV-Vis absorbance spectrum of cell-free ferredoxin is nearly identical to the published spectra for ferredoxin purified from the native organism Synechocystis sp PCC 6801 (Ref 3). The spectrum shifts upon addition of the reducing agent sodium dithionite, indicating the reduction of the iron-sulfur cluster (See Figure 14). The original spectra shape is recovered after re-oxidation of the iron-sulfur cluster by bubbling with air. Thus, reduction and re-oxidation can be repeated as expected for fully competent ferredoxin.

![UV-Vis Absorbance Spectrum of Purified Cell-free Ferredoxin](image)

**Figure 14:** UV-Vis absorbance spectrum of cell-free ferredoxin in oxidized, reduced and re-oxidized condition

Ferredoxin Conclusions. When supplemented with reduced iron and sulfur sources, our *E. coli*-based cell-free system contains all the factors necessary to form and install a simple iron-sulfur cluster into the protein ferredoxin. Maturation of ferredoxin is accomplished with approximately the same efficiency in the cell-free system at 37 °C as was achieved in *E. coli* at 28 °C. Matured cell-free ferredoxin was fully active and capable of passing electrons between known coupling agents. The information gained about the capabilities of the cell-free system and conditions favorable for iron-sulfur cluster formation is to be used toward folding of the more complex iron-sulfur protein hydrogenase.

Progress

Over the past year, we have made significant progress in developing molecular biology methods required for the efficient evolution of an oxygen-tolerant hydrogenase. We have also established, for the first time, that active proteins containing iron-sulfur centers can be produced in cell-free synthesis systems. However, we have yet to demonstrate success in producing an active hydrogenase. This will be the dominant
focus for next year’s research. In parallel, we have evaluated information in the literature relative to various feasibility issues for the overall direct conversion approach. We continue to be convinced that if we can develop an oxygen tolerant hydrogenase, hydrogen production economics are favorable for the biological conversion of sunlight to hydrogen.

**Future Plans**

2. Clone, express, and optimize activation of hydrogenases from blue-green algae.
4. Clone and express native hydrogenase into *Synechocystis* and test for hydrogen production.
5. Clone and express evolved hydrogenase into *Synechocystis* and begin to optimize hydrogen production rates and efficiencies.

**Publications**

No publications have been submitted to date. The cell-free ferredoxin expression work is now being prepared for publication. The molecular biology improvements are nearly ready for publication.

**References**

1) Peters, J.W. et al., X-ray crystal structure of the Fe-only hydrogenase (CpI) from *Clostridium pasteurainum* to 1.8 angstrom resolution, *Science* 282:1853,1998.

**Contacts**

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II. Project Results: Hydrogen

Part II: Metabolic Engineering of Hydrogen Production in Filamentous Cyanobacteria

Investigators
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Introduction
Since the engineering of an oxygen tolerant hydrogenase as described in Part I is a significant experimental challenge, we are exploring an alternative approach, in which we direct photosynthetic hydrogen production to an anoxic compartment (heterocysts) found in filamentous cyanobacteria (Figure 1). In filamentous cyanobacteria, photolytic water cleavage is separated spatially from oxygen-sensitive nitrogen fixation. Light-dependent oxygen release proceeds only in vegetative cells, whereas nitrogen fixation is restricted to the anoxic heterocysts (Fig. 1, upper panel). Within heterocysts, oxygenic photosynthesis is suppressed. This, together with other oxygen-scavenging mechanisms provides an anoxic environment for the proper functioning of nitrogenase. The remaining vegetative cells (Fig. 1, upper panel) can perform oxygenic photosynthesis, storing light energy into fixed carbon such as sucrose. The sucrose then can be transported into the heterocysts to fuel nitrogen fixation.

Anabaena variabilis

H₂-Producing Strain

Figure 1. Schematic illustration of photosynthesis and nitrogen fixation in filamentous cyanobacteria such as Anabaena variabilis (top panel). Proposed scheme for the conversion of Anabaena variabilis to a hydrogen-producing strain (lower panel).
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Results

**Hydrogenase expression vector.** The following plasmid, pNG180, (Figure 2) was constructed and described in the last progress report. It is a shuttle vector designed to express the hydrogenase gene, *shydA*, from *Clostridium pasteurianum* in *Anabaena variabilis*. Since the last report, several attempts were made to introduce the plasmid into *Anabaena variabilis* via triparental mating, direct transfer of DNA between bacteria. Exconjugants were selected on agar plates with chloramphenicol. No stable transformants were obtained after several trials. We suspected that the chloramphenicol resistance cassette did not express well in *Anabaena variabilis*. To correct the problem, we substituted the chloramphenicol resistance cassette with a kanamycin resistance cassette with a *psbA* promoter (Figure 3, unpublished, Peter Wolk, Michigan State University). This selection marker has been shown to work well in *Anabaena variabilis*.

![Figure 2: Hydrogenase expression vector.](image1)

Figure 2: Hydrogenase expression vector. The expression vector carries the nitrogenase promoter from the cyanobacterium, *Anabaena variabilis*, which will drive the expression of the hydrogenase gene from *Clostridium pasteurianum*. This arrangement will allow the hydrogenase to be expressed exclusively in heterocysts in a temporally optimal manner. *PnifH*, nitrogenase promoter; *shydA*, *Clostridium* hydrogenase gene; TT, transcriptional terminator; *oriV*, origin of replication; *oriT*, origin of conjugal transfer; *repB*, *repA/C*, replication proteins; *Cm*, chloramphenicol resistance cassette.

![Figure 3: New hydrogenase expression vector.](image2)

Figure 3: New hydrogenase expression vector. The *PpsbA::Km* cassette replaced the original chloramphenicol cassette in the new vector.

We are in the process of introducing the newly constructed plasmid with the new kanamycin resistance cassette, pNG 261, into *Anabaena variabilis*. 


Construct for Targeted DNA Replacement in *Anabaena variabilis*. Concerns with the stability of the above plasmid led us to take an alternative strategy to introduce the hydrogenase expression construct. Instead of carrying the expression construct on a plasmid, the construct will be integrated into the chromosome of *Anabaena variabilis*. The following plasmid (Figure 4), containing the *nif* operon from *Anabaena variabilis* was constructed. The hydrogenase expression construct will be inserted at the unique SwaI site.

**Figure 4:** Cloned *nif* operon from *Anabaena variabilis*. *nifH* is deleted. The hydrogenase expression construct will be cloned into the SwaI site.

**Helper Plasmid with DNA methyltransferase genes.** A DNA vector carrying three DNA methyltransferase genes from *Anabaena variabilis* has been constructed (Figure 5). This DNA vector will provide an important function to allow us to introduce DNA into *Anabaena variabilis* at high efficiency. In *Anabaena variabilis*, as in many bacteria, restriction enzymes are present to degrade foreign DNA as part of the natural defense mechanism against foreign or viral DNA. To enable our DNA constructs to enter the cyanobacterium at higher efficiency, we will use this DNA vector to pre-methylate DNA so it will evade Anabena’s DNA restriction system. Of the three DNA methyltransferase genes we cloned, *avaIIIM* did not appear to be functional. We have since obtained a functional equivalent (*ecoT22IM*) of *avaIIIM* from Peter Wolk, Michigan State University. We are now in the process of replacing *avaIIIM* with *ecoT22IM*.

**Progress**

Basic genetics tools (expression vectors, helper plasmid) have been constructed or in the final stage of assembly. These tools will be used to introduce genetic modifications into the genome of *Anabaena variabilis*. These genetic modifications (expression vector and mutations) will lead to alterations in the metabolism of the bacterium ultimately resulting in the inactivation of the nitrogen fixation pathway and the addition of a hydrogen evolution pathway.
II.1  Project Results: Hydrogen

Figure 5: Helper plasmid with three DNA methyltransferases from *A. variabilis*. pACYC ori, origin of replication; Tc, tetracycline resistance cassette; *avaIM*, *avaIIM* and *avaIIIM*, DNA methyltransferases from *A. variabilis*.

Future Plans
We will finish the modification on the helper plasmid. Also, we will test whether the newly constructed plasmids can be stably replicated in *Anabaena variabilis*. Once we have finished all the genetic modifications, we will test the final strain for hydrogen production.

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II.1.2 Nanoscale Electrochemical Probes for Monitoring Bioconversion Hydrogen

Investigators
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Introduction
The economic production of hydrogen remains one of the key issues for realizing the hydrogen economy. In response to this challenge, Professors Swartz and Spormann, are pursuing biological production of hydrogen as part of the GCEP hydrogen initiative. Our team works with Professors Swartz and Spormann to develop nano scale sensors to better understand the electro-chemistry of hydrogen production via bio-energy conversion. The sensors are designed to measure reduction-oxidation reactions, electron transfer reactions, and the broader kinetics of biochemical processing within the cell cytosol. The sensors we are pursuing may also be employed to determine membrane potentials across lipid bilayers. Considering the size of the cells we are investigating, which is less than 5 microns, we estimate that the size of the sensors must be at least one order of magnitude smaller. Therefore, we manufactured probes with a diameter of tens to hundreds of nanometers. We are integrating these sensors into a single cell diagnostic platform that is capable of mapping biochemical reactions inside single cells. (A schematic drawing of the experimental set up is shown in Fig.1).

Figure 1: Single cell diagnostic platform with electrochemical nanoprobes,
A: Electrochemical nanoprobes are mounted to an atomic force microscopic stage,
B: Localization of single cells is achieved with a planar patch clamp device,
C: For optical visualization a confocal fluorescence microscope is used.
II.1 Project Results: Hydrogen

Background

The impetus for the development of dynamic intracellular sensing probes comes from an increasing body of evidence substantiating the role of intracellular ion flux in cell metabolic control. Observing the dynamics of intracellular electrochemistry is crucial in creating a theoretical framework for understanding interactions between signaling mechanisms and reaction paths of bio-energy conversion within a single cell and also between networks of cells.

Today, the highest resolution tools investigating cell communication phenomena are cell attached capacitance measurements using patch clamps. The revolutionary insights provided by the ‘patch clamp’ sensor of Sakman, Neher, and Marty [1,2] furthered our understanding of transmembrane signaling mechanisms. However, still there is no capability to investigate electrochemical phenomena simultaneously at a variety of different cell locations and couple that data with force feedback measurements.

The purpose of these efforts is to develop a probe capable of electrochemically characterizing the cell membrane surface and the cell interior by piercing the cell while causing minimal damage. Previous research identified Scanning Electrochemical Microscopy (SECM), as an important analytical tool for studying surface reactions and their kinetics down to nano-scale dimensions. The use of this method has been demonstrated in a wide range of applications, such as resolving fast heterogeneous kinetics at various material interfaces or imaging of biological molecules. [3-5] The spatial resolution of SECM depends on shape and size of the electrochemical electrode. Ultra Micro Electrodes (UME), which are tip probes having sub-micron electrodes on the top, are required to obtain resolution at the nanometer scale. Manufacturing approaches have been investigated ranging from isolation of etched metal wires or Scanning Tunneling Electron Microscopy (STEM) tips for single electrode systems to batch fabrication strategies for electrode array systems.[6-9] A combination of SECM with other Scanning Probe Microscopy (SPM) techniques, such as Atomic Force Microscopy (AFM), is highly desirable in order to obtain electrochemical information as well as complementary surface information simultaneously. [10] In particular, the combined use of SECM and AFM will allow for precise positioning of probes adjacent to or inside of cells and sensing of concentrations and fluxes of electrochemically active substances. A crucial component of such a system is the specialized probe system that has to be composed of a micro-mechanical cantilever structure necessary for the AFM mode and an electrochemical UME-tip required for a high performance SECM. Several strategies for fabrication of such transducer structures have already been reported. [11-16] While these efforts resulted in functional tip structures and combined AFM and SECM imaging, performance issues related to the tip sharpness, low aspect ratio of the tip structure, and size of the electrochemical electrode remain. The commonality for most of the above described fabrication technologies is a single electrode production scheme, which limits miniaturization potential and fabrication of multi-electrode systems. In order to overcome these limitations, enable radical miniaturization, and build high density array probes, fabrication schemes exploiting micro- and nano-fabrication technologies have been developed.
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Figure 2: A) Fabrication of HARS tips: 1 Patterning of a silicon oxide etch mask, 2 Isotropic silicon etching to shape the tip and Deep-RIE Si-Etching to shape the shaft, 3 Releasing silicon oxide caps and sharpening of tips by oxidation and back etching of silicon oxide, 4 finished HARS tip, B) Embedding of HARS tips in silicon nitride and metal patterning of the electrode system: 5 Growing of silicon oxide and silicon nitride, 6 Back-etching of the silicon nitride using non uniform resist coating on high- aspect ratio structures and release of oxide layer using wet etching, 7 Patterning of the electrode system utilizing lift-off technique, 8 Isolation of the electrode system and tip structure with deposition silicon nitride. C) Fabrication of UME’s and cantilevers: 9 Shaping of cantilevers, 10 FIB-patterning of etch metal mask, 11 Etching of the isolation layer exposing the electrode metal layer (Creation of UMEs) and patterning of back side etch mask for release, 12 Releasing of cantilever structure using wet etching.

Results

Micro- and nano-fabrication technologies originate from the field of microelectronics, combining parallel processing techniques with a miniaturization potential of sub micron regimes. In particular, high-aspect ratio electrochemical tip probes embedded in silicon nitride cantilevers have been developed for simultaneous AFM and SECM analyses.
II.1 Project Results: Hydrogen

[9,17] The fabrication process is based on batch processes in combination with an etch-mask technology utilizing FIB techniques to achieve both well defined UME and sharp high-aspect ratio tips on a single cantilever as well as in cantilever arrays. The process has been developed on four-inch wafers and is divided into three main fabrication pathways. An overview of the fabrication process is depicted in Fig. 2.

First, High-Aspect Ratio Silicon (HARS) tips are shaped combining isotropic etching with an anisotropic Deep-RIE-silicon etch process. Second, silicon tips are embedded in a silicon nitride layer, electrode systems are patterned and passivated with an isolation layer. Finally, a UME on top of the tip structures is established by etching the isolation layer only at the tip. To achieve accuracy and resolution in the nanometer regime on the HARS tip, an etch mask technology has been developed utilizing a focused ion beam-based technique. Subsequently, the cantilevers with embedded electrochemical tip electrodes are shaped and released. A detailed description of the whole fabrication process can be found in previous publications.[9,17]

Figure 3: Tip-probes at different fabrication levels A) Example of an etched HARS tip B) Detail of a sharpened tip with a tip radius smaller than 50 nm C – D) HARS tips embedded in a 500 nm thick low stress silicon nitride E - F) Metallized embedded HARS tips.
In Fig. 3A, an example of a finished HARS tip is shown. Tips with a shaft diameter of 1.2 µm are created using oxide caps as a mask.[9,18] HARS tips with an aspect ratio of up to 20 and a diameter in the sub micron regime can be fabricated in this way. Fig. 3B shows a detail of a sharpened tip with a tip radius smaller than 50 nm. HARS tips embedded in a 500 nm thick low stress silicon nitride are shown in Fig. 3C and D. Application of a non-uniform coating of photo resist in combination with silicon nitride etching allows for the exposure of the silicon tips. [17,19] About 5 µm of the silicon tip at its base is anchored in the silicon nitride while the rest of the tip protrudes from the nitride layer. This processing step results in an additional reduction of the tip diameter to 600 nm and creates further sharpening of the HARS-tip.[28] In Fig. 3E and F, a platinum electrode structure is patterned on the embedded tips. Using magnetron sputtering, a homogeneous metal layer is formed and sufficient side-wall coverage of the HARS tip structures is observed.

**Figure 4:** SEM pictures of a finished tip probe array A) Tip probe array with four UME cantilever structures  B) Tip probe of the cantilever structures with a platinum UME (radius of 200 nm).

**Figure 5:** Optical low magnification micrographs of an SECM-AFM probe device.
This conformal metallization establishes a reliable electrical connection between an electrode on top of the tip and bonding structures on the bulk silicon. This process is not limited to single electrode patterning and can be expanded to larger linear arrays as well as to two-dimensional arrays. UME’s on top of the tips are recognizable in Fig. 4B. The UME diameter of these probes is about 200 nm. A finished tip probe array is depicted in Fig. 4A. The bending of the cantilevers is caused by small residual stresses resulting from the nitride thin film passivation layer. The probes are used for the electrochemical characterization. A low magnification optical micrograph shows a probe device with an array of four cantilever tip probes and its bonding pad system (Fig. 5).

**Electrochemical Characterization**

Electrochemical characterization is carried out using a Solatron 1287, an electrochemical interface, in combination with a Solatron 1260, Impedance/Gain Phase Analyzer (Solatron Analytical). As shown in Fig. 6, a three-electrode arrangement was employed. The cantilever device is mounted on a micromanipulator stage (PCS-6000, Burleigh Instruments) or Atomic Force Microscope (Picoplus, MI). The tips on the cantilever are immersed and positioned in a drop or film of electrolyte in a controlled fashion. A platinum thin film layer is used as a counter electrode and an Ag/AgCl wire electrode functions as the reference electrode. Cyclic voltammetry of the tip probe electrode with a platinum wire reference electrode is used to characterize the electrochemical behavior of the tip probes. In these experiments, phosphate buffer is used as an electrolyte solution.

The tip probe system shows all the important electrochemical surface reactions of a platinum electrode in a phosphate buffer solution. Hexaammineruthenium (III) chloride is used to study the response of the electrode in a reversible redox system. Fig. 7 shows voltammograms taken in an electrolyte with 10mmol and 0mmol concentration of Ru(NH₃)₆³⁺. The tip probes in these experiments have an approximate electrode area of 0.125 µm². The reduction current appears in the potential regime below –200 mV related to Ag/AgCl at 0.1 mol KCl. Electrochemical Impedance Spectroscopy (EIS) analysis leads to a faradic impedance of the tip transducer system at a DC working potential of ~300 mV of $5 \times 10^7$ Ohm for 10mM Ru(NH₃)₆³⁺ and $4 \times 10^9$ Ohm for phosphate buffer only. Both, the behavior of the reduction current and values of the faradic impedance in a Ru(NH₃)₆³⁺ redox system shows typical characteristics of a single ultra micro electrode in sub micron size and indicate the electrochemical functionality of the tip probe system.

This electrochemical, platinum, nano-sized transducer system can be directly applied to measure ion fluxes or electrochemically active species within and between cells. Furthermore the transducer system can be modified to detect specific ions such as sodium, potassium, or substances involved in cellular metabolic reactions or signaling pathways.[21]
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Figure 6: Schematic electrode arrangement of an electrochemical measurement set up.

Figure 7: Cyclic voltammograms of tip probe with a platinum UEM (0.125 µm²) in 0.1 M Phosphate buffer electrolyte and in a 10 mmol Ru(NH₃)₆Cl and 0.1 KCl solution. The potential is related to a 0.1 M KCl Ag/AgCl-Reference electrode, Potential sweep rate was 10 mV/s.

Silicon nitride cantilever array with single tips and tip arrays

Obtaining measurements with high spatial resolutions requires increased probe densities. Arrays of multi-probe systems on a single cantilever were designed and fabricated as shown in Fig. 8. Silicon tips with spacings of 10 micrometers are embedded in silicon nitride pillars and supported by a 500 nanometer thick silicon nitride cantilever. The electrically conductive tips are connected separately to the monitoring system such that individual signals from each tip can be transmitted. The metal lines are sputtered on an isolated substrate surface and covered with another insulation layer to define the UME on the tip of the probe structure as described previously. The cantilever and its substrate are compatible with conventional AFM (Atomic Force Microscope) systems. The probe or probe array can be mounted onto an AFM scanner to take advantage of the precise closed-loop motion control and force feedback data of the AFM system.
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Figure 8: A) Silicon nitride cantilever array with single high-aspect-ratio tips. The thickness of cantilevers is about 500 nm B) High-aspect-ratio tip array on single silicon nitride cantilever.

Figure 9: A) multi-array ultra sharp silicon tips fabricated with a combination of two plasma etching steps. B) a closer look of the individual silicon tip with a radius less than 20 nm

Multiple arrays of ultra sharp high-aspect-ratio silicon tips

Multiple arrays of ultra sharp nano-tips with tip radii as small as 20 nanometers are currently being fabricated by combining two plasma etching processes on single crystalline wafers. As shown in Fig. 9, nano-tips located on top of the pillars respectively have an aspect ratio of over 10:1. Such a high density of ultra sharp tips represents a potentially powerful tool for measuring cell properties in real time. The tips can be inserted into cells such that multiple electrodes are present within a single cell or with a
single tip in adjacent cells. The electrically active tips will be individually connected by conductive vias to CMOS transistors on the back-side of the wafer. In this way, both individual addressability and signal processing are achieved.

The tip is defined, so that most of the tip is insulated and only a small region at the top has an exposed metal electrode. This will provide a well defined tip geometry with nanometer dimensions to further assure localized measurements of dielectric behavior within the cell interior. The fabricated nano-tip arrays on cantilever structures integrate well with the AFM stage for precise positioning relative to cell surface and subsequent penetration of the cell membrane.

Figure10: A 40µm-diameter ETWI consisting of four 2µm-thick poly-silicon layers and four 1µm-thick thermal silicon-oxide layers  A) SEM image of the cross section B) SEM image of the top view (poly-silicon and silicon appears as dark, silicon-oxide appears as bright) and C) Optical microscope image of the top view (poly-silicon and silicon appears as bright, silicon-oxide appears as dark).
Fabrication of silicon Via Structures

Limitations of connection density of current technologies are imposed by space restrictions resulting from designing and fabricating both connection structures (bonding pads, flip chip pumps) and functional devices (MEMS or CMOS) on a single wafer side. In order to overcome these limitations and open the use of both sides of a wafer independently, electrical through-wafer interconnections are necessary. The through wafer interconnection concept is based on multi-layer deposition techniques. Openings in a double-sided polished wafer are created by applying a high-density inductively coupled plasma (ICP) etch technique.[22] Hole structures with a diameter of 20 µm are formed through a 350-µm thick wafer. A multi-layer system of up to eight layers consisting of alternating conducting layers (N-type doped poly-silicon) and isolating layers (silicon-oxide) are grown until the vias are filled. The silicon-oxide and poly-silicon layers are grown using a low pressure chemical vapor deposition process to achieve a high deposition uniformity. Subsequently, all layers on the wafer surface are removed in a chemical mechanical polishing process. In this way, a multi-connection, through-wafer structure can be fabricated. Fig. 10 shows an example of such a multi-layered interconnection structure. The applied low-pressure chemical vapor deposition techniques guarantee a sufficient homogenous coating outside and inside of the entire structure to a minimum layer thickness of one micrometer. The connection quality has been examined combining impedance spectroscopy and focused ion beam technology. Depending on the geometry and the doping profile of the poly-silicon layers, a connection resistance of less than 80 Ohms can be achieved with sufficient DC isolation. This technique is compatible with high temperature processes and is suitable for MEMS as well as CMOS applications.

Figure 11: Ultra-sharp planer silicon nitride tip fabricated with a combination of micro-fabrication technique and FIB (Focused Ion Beam) techniques penetrating individual cells.
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Progress

The developed probe systems can contribute to a fundamental understanding of cell signaling mechanisms and reaction schemes of bio-energy conversion at unprecedented levels of spatial and temporal resolutions. Fig. 11 shows an example of a tip probing individual cells with an ultra-sharp planer silicon nitride tip probe.

These unique analytical tools are applicable to a variety of important scientific questions related to energy conversion strategies without the production of carbon compounds as a by-product. One example is the investigation and verification of electrochemical reactions, electron transfer mechanisms, and their kinetics of genetically modified bacterium cells on a single cell level. The developed measurement set-up allows for an investigation of effects due to genetical modification of cells and helps to effectively engineer a cell system specializing in a clean generation of molecular hydrogen.

Further, the transducer system can be applied to study bio-energy conversion processes with a highest spatial resolution in cells or, ultimately, in energy converting cell organelles such as the mitochondria.

Furthermore, this developed probe system is not only applicable to the investigation of hydrogen generation processes but also applicable to the exploration of new technologies for hydrogen utilization. In particular, this probe system is well suited for studies of electrochemical conversion reactions and their opportunity in terms of efficiency and low cost of fuel cells at sub micrometer scale. These investigations are currently pursued for the GCEP project "Micro and Nano Scale Electrochemistry applied to Fuel Cells".

The development of this new class of electrochemical nano-probes enables us to provide a unique tool to explore reaction paths, characterize material properties at nano scale for both generation and utilization of hydrogen in a clean and efficient fashion.

Future Plans

An electrochemical cantilever transducer system with platinum electrodes in sub micron regimes was developed. Electrochemical investigations showed full functionality of the probe system. Due to the high aspect ratio topography of the tip structure and low spring constant of silicon nitride cantilevers, these probes are particularly well suited for combined high-resolution SECM and AFM analysis in living cells.

Next year the probe system in combination with the single cell diagnostic platform (Fig.1) will be applied for:

- Study of genetically modified cells for clean hydrogen generation.
- Study and exploration of energy conversion reaction in energy converting cell organelles such as mitochondria.

Further, the probe system will be applied for:

- Study of electrochemical phenomena at nanometer scale of fuel cell for an efficient and low cost hydrogen utilization.
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Publications

References
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II.1.3 Micro and Nano Scale Electrochemistry: Application to Fuel Cells

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Introduction
Fuel cells offer the tantalizing promise of cleaner electricity with less impact on the environment than traditional energy conversion technologies. This is because fuel cells are direct electrochemical energy conversion devices. In other words, they convert chemical energy, in the form of a fuel and oxidant, directly into electrical energy. Contrast this to combustion engines, which first convert chemical energy into heat, heat into mechanical energy, and finally mechanical energy into electricity.

Widespread fuel cell viability will not occur without further technological breakthroughs. The emerging domain of nanoscience and technology may provide solutions. As identified in a U.S. Government report[1] on basic research needs for the hydrogen economy, nanoscience introduces powerful and virtually untapped new dimensions to fuel cell research.

Why should nanoscience be so beneficial to fuel cells? The answer comes from a deeper understanding of the fundamental principles involved in the electrochemical generation of electricity. Fuel cells produce electricity by converting a primary energy source (a fuel) into a flow of electrons. This conversion necessarily involves some sort of energy transfer step, where the energy from the source is passed along to the electrons constituting the electric current. This transfer has some finite rate and must occur at an interface or reaction surface. Thus, the amount of electricity produced scales with the amount of reaction surface area or interfacial area available for the energy transfer. Larger surface areas translate into improved performance. Unsurprisingly, then, the desire for large surface areas has led to a focus on nano-materials. A cube of material measuring 1 nm per side has $10^6$ times greater surface to volume ratio compared to a cube of material measuring 1 mm per side. In addition, to increasing the ‘outside’ surface area of a particle by decreasing its dimensions one can also increase ‘internal’ surface area by introducing atomic defects such as dislocations to enhance species diffusivity and chemical reactivity.

Despite recent technological successes wrought by the clever incorporation of nano-structured materials in fuel cells, we are still far away from possessing a solid scientific understanding of what is really going on at the nano-scale. Many critical questions remain. For example:

- What are the characteristic dimensions over which energy transfer or charge transfer reactions can effectively occur?
- Is there such a thing as too small? If the periodicity of a nano-structured interface is smaller than the characteristic energy transfer dimension, the answer may be yes.
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• How exactly do kinetic properties scale at small dimensions? Is there more than simple surface area scaling at work?

Studying the kinetic scaling behavior of nano-structured systems can be quite complicated. In fuel cell systems, for example, it has long been believed that the oxygen reduction reaction (ORR) can only occur at confined spatial regions, called “triple phase boundaries” (TPB's) where the electrolyte, gas, and electrically connected catalyst particles contact. However, the reaction-zone structure of a state of the art fuel cell is complex, consisting of a porous, heterogeneous mixture of conductive carbon powders and platinum particles, often mixed with a solid polymer electrolyte binder. Due to this complexity, the true amount of TPB in a fuel cell is difficult, if not impossible, to determine. Thus, the relationship between catalyst microstructure (i.e., TPB geometry) and fuel cell performance is still unclear.

In order to begin answering some of these questions, this research pioneers several novel micro and nano-scale electrochemical techniques, which are used to study fuel cells at the sub-micron length scale. As a first approach, we have developed a technique that employs platinum microelectrodes to examine the TPB properties of polymer electrolyte fuel cells. By constructing reproducible, geometrically simple, well-defined electrocatalyst structures of various sizes, a relationship between electrocatalyst geometry and electrochemical behavior is clearly delineated. This study provides perhaps the most direct experimental validation to date of the TPB theory.

Extending our characterization ability to the nano-scale, a second technique, called AFM impedance imaging is also developed. The AFM impedance imaging technique allows highly localized measurements of electrochemical properties to be acquired across sample surfaces.

While the techniques presented in this report have been successfully employed to study the electrochemical behavior of fuel cells, characterizing and understanding nano-structures is a challenge that extends far beyond the fuel cell realm. Many other devices, such as solar cells, sensors, and thermoelectric converters also benefit from nano-structured materials. The parallels between these systems and fuel cells make them highly amenable to the same type of nanometer scale visualization and measurement techniques, offering rich opportunities for further research.

Background
The O₂/Nafion/Pt Triple Phase Boundary

The idea of the triple phase boundary (TPB) is extensively employed in the fuel cell literature, especially with respect to solid oxide fuel cells (SOFC's) and polymer electrolyte membrane fuel cells (PEMFC's). The TPB concept holds that hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR) can only occur at confined spatial sites, called “triple phase boundaries” (TPB's) where electrolyte, gas, and electrically connected catalyst regions contact. A simplified schematic of the TPB is shown in Fig.1. The reaction kinetics (especially the ORR kinetics) often present a significant limitation to fuel cell performance. Therefore, understanding, characterizing,
and optimizing the TPB content in fuel cells provides excellent opportunities for performance enhancement.

![Figure 1: A simplified schematic diagram of the electrode/electrolyte interface in a fuel cell, illustrating the triple phase boundary reaction zones where the catalytically active electrode particles, electrolyte phase, and gas pores intersect.](image)

On the technology side, efforts to increase the amount of TPB in technological fuel cells with nano-structured catalyst-layers have proven highly successful. By employing nano-scale composites of catalyst material, conductive support, solid-electrolyte, and gas pore space, investigators have been able to dramatically increase the amount of TPB, thus improving kinetic performance.[2,3]

From a scientific perspective, recent efforts have been made to more clearly delineate the nature and properties of the TPB. Most of this work has been focused on SOFC’s[4-8], with very few studies directed towards PEMFC’s[9]. However, in all cases, there is a growing realization that the simple concept of the TPB as a singularity is unrealistic; rather, it should be thought of as a “zone”, whose width, properties, and behavior depend on a complex interplay between coupled reaction and diffusion processes.

**AFM Impedance Imaging**

An ultimate tool for the rapid development and understanding of fuel cells and other energy conversion devices would be an imaging system that allows researchers to visualize the fundamental physical processes at work in the conversion of energy at the micro or nano scale. The development of such a tool embodies a major part of our research, and we report on steps towards this goal with the design and demonstration of an AFM impedance imaging system. The AFM impedance-imaging system permits spatially resolved electrochemical studies at the nanometer scale. First validated on simple test devices, the AFM technique is then applied to investigate sub-micron details of Nafion fuel cell electrolyte films and nano-scale platinum catalysts. The impedance imaging technique makes use of the scanning capabilities of the AFM to acquire 2-dimensional *images* of impedance across sample surfaces. While the potential of the system is demonstrated by application to electro ceramics and fuel cell systems, it is expected that nanometer scale visualization and measurement of impedance will be valuable for a wide variety of materials investigations, including solid electrolytes, semiconductors, solar cells, electro ceramics, coatings and corrosion research, and Li-ion battery and fuel cell systems.
Impedance spectroscopy (IS) is a key characterization tool in the research and development of diverse materials systems. In fuel cell and battery research, it has been used to distinguish between various sources of cell loss; for example ohmic losses in the electrodes and electrolyte, activation overpotentials due to reaction kinetics, and mass transport effects. While these measurements resolve electrochemical phenomena *mechanistically*, they cannot resolve the phenomena *spatially*. In other words, standard IS measurements produce bulk, or system averaged results.

Recently, several spatially resolved impedance techniques have been developed. Fleig et al.\[10,11\] have used patterned arrays of microelectrodes to acquire spatially resolved impedance data from polycrystalline ceramics with a lateral resolution of 15 to 20 µm. Issacs et al. and others\[12-14\] have demonstrated localized electrochemical impedance spectroscopy (LEIS) methods (now commercialized) that function in an aqueous electrolyte and are capable of acquiring impedance data with a resolution of about 30 µm. Most recently, Pilaski et al.\[15\] have developed a scanned technique based on a capillary liquid-electrolyte droplet cell with an apparent resolution of around 100 µm.

In contrast to these methods, the atomic force microscope (AFM) impedance imaging technique introduced in this report leverages the capabilities of an AFM to acquire impedance images with sub 100 nm resolution. Furthermore, the technique is designed to measure all solid-state materials systems. The system is constructed from a commercially available AFM coupled to impedance measurement hardware (Fig. 2a). The AFM tip, which must be conductive, serves as the probe electrode for the IS measurements. Successive measurements across a sample surface are obtained by moving the AFM tip. Due to the time requirements for impedance acquisition, measurements are currently obtained in a point-by-point fashion rather than in a continuous scanning manner. Single frequency or complete impedance spectra can be obtained during the scans. Custom developed software automates the communication and synchronization between the hardware systems.

**Figure 2:** Schematics of the experimental configurations used in this study for AFM impedance imaging. **a**) General concept of AFM impedance imaging. Impedance is measured between a local probe (the AFM tip) and a bulk electrode. A significant spreading resistance contribution at the AFM tip/sample contact point ensures local characterization. (Shown schematically by the hemispherical lines.) **b**) Experimental configuration for the Au/Si₃N₄ test structures. The gold lines (black) are connected to the bulk electrode. If the AFM tip scans over the gold regions, an ohmic response should be obtained. **c**) Configuration for the Nafion characterization experiment. The impedance is
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measured between an AFM tip on the Nafion top surface and a bulk bottom electrode (a reversible hydrogen electrode) which is hermetically sealed and supplied with hydrogen gas.

AFM electrical property measurements are not new. Scanning spreading resistance microscopy[16-18] (SSRM), conductive or current sensing AFM[19-21] (C-AFM), and tunneling-AFM[22,23] (TUNA) allow DC-characterization of materials. Other techniques make use of the long-range electrostatic forces between a sample and a conductive non-contact AFM tip to extract surface potential images[24,25] (scanning surface potential microscopy, SSPM) or capacitive information on semiconductor oxide surfaces[26-28] (scanning capacitance microscopy, SCM). Layson et al.[29] have obtained AC impedance data on poly(ethylene) oxide films directly through a conductive AFM tip at individual points on the film surface, but do not report impedance imaging. Recently, Kalinin and Bonnell[30,31] have reported a scanning impedance microscopy technique (SIM) that detects the phase change in a conductive non-contact cantilever as a lateral bias is applied to a sample of interest. This technique in combination with SSPM, is shown to be useful for the determination of AC transport properties across lateral interfaces. In the SIM technique, the voltage perturbation is not applied through the tip, but rather between macroscopic electrodes on the substrate. Shao, Kalinin, and Bonnell[32] have even more recently reported a contact version of SIM, using a similar technique to acquire localized impedance that we report here. Our contribution represents a significant elaboration on the details, capabilities, and limitations of the AFM impedance imaging technique, as well as an extension of the technique to the electrochemical and ionic domain.

Results
The Oxygen/Nafion/Pt Triple Phase Boundary

As detailed in the introduction and background sections to this report, there is a significant correlation between catalyst microstructure and performance in fuel cells. Specifically, it has been theorized that fuel cell performance depends strongly on the triple phase boundaries (TPB's) for the fuel cell reaction.

While many researchers have theorized on the existence and the importance of TPBs in fuel cell electrochemical reactions, there is very little actual experimental evidence for the role of TPBs in PEM fuel cells. In this report, a first ever detailed systematic study of the Air/Platinum/Nafion triple phase boundary is described, which attempts to elucidate the true nature, electrochemical properties, and scaling characteristics of TPBs in PEM fuel cell environments.
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Figure 3: a) Electron micrograph of a series of Pt-microelectrodes directly patterned via FIB onto the surface of a Nafion membrane “half-cell” MEA. b) Higher magnification electron micrograph of a portion of an FIB patterned array of 1µm radius Pt-microelectrodes. After array patterning is complete, the electrodes are electrically interconnected with a series of FIB deposited Pt wires (not shown).

The TPB investigation is accomplished via the fabrication and measurement of micro-sized, simplified fuel cell catalyst geometries, such as the disk-shaped catalyst features pictured in Fig. 3. The micro-scale platinum features pictured in Fig. 3 are fully functioning fuel cells. Truly micro fuel cells, they may in fact be some of the world’s smallest PEMFCs ever evaluated. Fig. 4(a) shows the absolute I-V curves for three different circular fuel cells with radii varying from 10-40µm. The absolute performance of these tiny fuel cells is insignificant; note the small values for current. Not surprisingly, the larger the fuel cell, the greater absolute current it delivers. Fig. 4(b) reports the results from the same three circular Pt-structures, but now normalized by area; on an area-normalized basis these results argue that smaller fuel cells are better. Intriguingly, the I-V curves of the three fuel cells are roughly comparable if they are scaled relative to their circumferences, rather than their areas, as shown in Fig. 4(c).
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Figure 4: I-V curves for a series of Pt-microelectrodes operating as hydrogen-air fuel cells. (Heavy Line) 40µm radius microelectrode. (Medium Line) 30µm radius microelectrode. (Thin Line) 10µm radius microelectrode. a) Absolute current vs. voltage. b) Current density vs. voltage. c) Perimeter normalized current density vs. voltage.

In order to understand this scaling phenomenon, it is necessary to consider the fundamental electrochemical characteristics of the Pt-catalyst structures. A systematic impedance study allows us to separate the contributions of electrolyte resistance ($R_e$) and Faradaic impedance ($R_f$) of the oxygen reduction reaction (ORR). The results of this study are given in figures 5(a) and 5(b). As Fig. 5(a) reveals, $R_e$ for the Pt-electrode structures is proportional to $r^{-2}$ for large area electrodes and proportional to $r^{-1}$ for small area electrodes. For small electrodes (when the electrode size, $r$, is much smaller than the electrolyte thickness, $t$) the measured electrolyte resistance, $R_e$, can be shown to be inversely proportional to the electrode radius:\[33\]:

\[
R_e = \frac{\rho}{4r}, \quad r << t
\]  \hspace{1cm} (1)

Whereas for $r>>t$, the resistance is inversely proportional to the electrode area:

\[
R_e = \frac{\rho \cdot t}{\pi r^2}, \quad r >> t
\]  \hspace{1cm} (2)

Thus, Fig. 5(a) relates a purely geometrical effect owing to the transition from an area-related electrolyte resistance for $r>>t$, to a point contact dominated spreading resistance for $r<<t$. This transition is recovered in the results of a simple finite element simulation (Fig. 6). In fact, the Nafion properties can be extracted by fitting the data to the simple finite element simulation, as shown by the dotted line in Fig. 5(a). A
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A parametric best fit of the finite element simulation to the experimental data is obtained for simulation values of Nafion thickness $t=90\mu m$ and Nafion resistivity $\rho=3000\Omega cm$. (Nominal reference values for dry Nafion 115 are $t=125\mu m$, $\rho=10-100\Omega cm$.[34-36]) Since the electrolyte in our experiments is subjected to a desiccating high vacuum environment prior to electrochemical measurement, it is unsurprising that our experimentally fit resistivity values are high.

**Figure 5:**

- **a)** Electrolyte impedance ($R_e$) vs. Pt-microelectrode radius. (♦) Experimental data from FIB patterned Pt-microelectrodes. (■) Experimental data from large-area shadow mask sputtered Pt electrodes. (---) Model fit based on finite element simulation. Solid lines and equations show slope $\approx 1$ for ($r < 100\mu m$), slope $\approx 2$ for ($r > 100\mu m$)
- **b)** Faradic impedance ($R_f$) vs. electrode radius. (♦) Experimental data from FIB patterned Pt-microelectrodes. Dashed lines and equations show slope $\approx 1$ for ($r < 40\mu m$), slope $\approx 2$ for ($r > 40\mu m$)

Perhaps more surprising are the results in Fig. 5(b), which show that $R_f$ is also roughly proportional to $r^{-2}$ for large electrodes and proportional to $r^{-1}$ for small electrodes. Note first that the Faradaic impedance is several orders of magnitude larger than the electrolyte impedance. This indicates that $R_f$ for the ORR dominates the electrochemical behavior of these circular micro fuel cells. (The losses from $R_e$ are negligible in comparison.)
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Figure 6: Field simulation results from the finite element model showing the transition from spreading resistance dominance for \( r \ll t \) to a uniform-field area-based resistance for \( r \gg t \).

For electrodes smaller than about 40\( \mu \)m, we see a direct relation between Pt-microelectrode circumference and \( R_f \). This expected result indicates that the ORR kinetics are scaling with the length of the TPB. As hypothesized earlier, the 2\( \mu \)m thickness of the catalyst structures prevents the bulk of the electrode area from participating in the ORR process. Instead, only the perimeter participates as active TPB for the Faradaic reaction. Interestingly, for microelectrodes greater than 40\( \mu \)m, the ORR kinetics no longer scale with a circumferential based TPB length. The roughly \( r^2 \) dependence for the larger Pt-electrodes is believed to arise from a cracking process due to the dimensional instability of the Nafion electrolyte. Post-mortem electron microscope analysis of Pt-microelectrodes confirms that cracking typically occurs for electrodes greater than about 40\( \mu \)m. (See Fig. 7)

Figure 7: a) A typical 10\( \mu \)m radius FIB patterned Pt-microelectrode imaged after testing under ambient conditions. Despite the vacuum-ambient-vacuum cycling the microelectrode remains intact. b) A typical 40\( \mu \)m radius FIB patterned Pt-microelectrode imaged after testing under ambient conditions. After the vacuum-ambient-vacuum cycling the microelectrode exhibits cracking.
The cracking is believed to be due to the expansion of the Nafion electrolyte upon removal from the vacuum environment and exposure to ambient humidity. This area distributed cracking introduces additional TPB sites in the larger electrode structures, which should scale roughly proportional to electrode area. For Pt-electrodes smaller than 30µm, no cracking is observed. For these small, unblemished electrodes, then, it is possible to extract a Faradaic resistance per unit TPB length ($R_{TPB}$). $R_{TPB}$ is calculated as:

$$R_{TPB} = 2\pi*r*R_f$$

From the data in Fig. 5(b), $R_{TPB}$ can be estimated at roughly $R_{TPB} = 6*10^9$ Ωµm.

As noted earlier, the Faradaic impedance dominates the electrochemical behavior of these micron-sized catalyst structures ($R_f >> R_c$). Thus, catalyst structures with an increased TPB length per unit area should show proportionally improved electrocatalytic performance. In Fig. 8, a uniform 40µm x 40µm square electrode is compared to a sectioned 40µm x 40µm square electrode. The two electrodes have the same total Pt area, but the sectioned electrode has 5 times greater TPB length. (Each interior section contributes 2 lengths of TPB.) As the impedance spectra for the two structures clearly show, the Faradaic resistance of the sectioned electrode is about 1/5 that of the uniform electrode. Not only do the Faradaic impedances for the two structures scale qualitatively as predicted, but the absolute quantitative values for the two structures scale almost exactly as predicted using the previously determined Faradaic resistance per unit TPB length, $R_{TPB} = 6*10^9$ Ωµm. This result grants at least some confidence that the TPB properties derived from the circular microelectrodes can be used for other geometries.

**Figure 8:** EIS Nyquist spectra and corresponding micrographs for two FIB patterned ‘artificial Pt-catalyst microstructures’ showing the direct relation between faradic impedance and TPB length. **a)** 40µm square Pt-catalyst structure sectioned into 25
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separate 8µm x 8µm squares. Electrical contact between the 25 sections is assured by the Pt interconnect wires. The sectioned structure shows a Faradaic impedance of around 8 MΩ. b) Undivided 40µm square Pt-catalyst structure. This undivided electrode shows a Faradaic impedance of around 40 MΩ. The two electrodes are imaged at a 53° angle, thus because of foreshortening they do not appear square.

Having determined a quantitative value for the resistance per Pt/Nafion triple phase boundary length, we can also infer TPB density requirements for a high performance PEMFC. For most fuel cell requirements, a cathodic ORR resistance of around 0.15Ωcm² is acceptable[37]. This implies a TPB density on the order of 10⁶ cm/cm². Assuming plane packed spherical platinum particles, each of which contributes an average TPB on the order of its projected circumferential length, this suggests an average catalyst particle size smaller than 30 nm is necessary to achieve the required ORR resistance.

AFM Impedance Imaging

The hope of an AFM impedance imaging system is the ability to directly visualize and correlate relationships between microstructure and performance for fuel cells and other alternative energy conversion devices at the sub-micron length scale. While this is the ultimate goal, intermediate proof of the 2D AFM impedance-imaging concept has first been demonstrated using specially developed micro-scale gold test patterns. (Experimental configuration follows Fig. 2b.) Representative impedance modulus ($Z_0$) and impedance phase ($\theta$) images obtained from the test patterns are compared to their topographic counterparts (topography deflection images) in Fig. 9. Note that the phase angle for the gold region is close to zero, indicative of ohmic transport, while the phase of nitride is close to –90°, indicative of capacitive behavior. (Mean phase values for the gold and nitride regions are -0.09° and -88°, respectively.) Note that at the 1µm scale, the boundary between the nitride film and the gold is more clearly resolved by the impedance image than the topography image. Full impedance spectra taken at several points on the sample (points A-E in Fig. 9) confirm the ohmic response of the gold and the capacitive behavior of the nitride (Fig. 10).
Figure 9: Topographical deflection (top row), Impedance modulus (middle row) and Impedance phase (bottom row) images from a gold/silicon nitride test pattern. Images increase in magnification from left to right. Images acquired according to the experimental configuration from Fig. 2b). Topographic deflection at 2Hz scan speed, 512 x 512 resolution. Impedance modulus and phase acquired at 1000 Hz, with a 10 mV excitation signal and 0V DC bias.
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Figure 10: a) Bode impedance modulus spectra and b) Impedance phase spectra acquired at specific locations (A-E) on the gold/nitride test pattern. The measurement locations (A-E) are denoted on the 10 µm impedance modulus image in Fig. 9. Spectra from the gold film show ohmic behavior, while spectra from the nitride region show a capacitive response. The impedance spectra were acquired from 100kHz-100mHz with a 10 mV excitation signal and 0V DC bias.

As indicated by the color-scale, the impedance images in Fig. 9 show an apparent binary contrast between the gold and the nitride. The mean impedance of the gold is around 5000Ω, while the mean impedance of the nitride is $4 \times 10^6$Ω. If the image contrast is adjusted so that variations at the low-end of the impedance range are visible, (Fig. 11a) further detail is resolved. Slight impedance variations, possibly due to changes in the thickness and topography of the gold film at the boundary with the nitride region, are apparent. Similar contrast adjustments at the high-end of the impedance range allow variations in the nitride film to be seen (Fig. 11b). The true impedance of the nitride film exceeds the measurement capabilities of our instrument at 1 kHz. Therefore, it is believed that these apparent variations in the nitride film impedance are simply a visualization of the error and noise structure of the instrument.
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Figure 11: a) Impedance modulus image from a 1µm area of the gold/nitride test pattern, scale adjusted to show the contrast details in the gold film impedance. b) The same impedance modulus image scale adjusted to bring out the contrast details in the nitride film impedance. The apparent nitride film details are likely associated with the noise structure of the instrument. Images acquired at 1 kHz with a 10 mV excitation signal and 0V DC bias.

A practical example of AFM impedance imaging in the electronic domain is provided by a study of grain/grain boundary transport in commercial polycrystalline ZnO varistors. Following Fig. 2a), the impedance of a cross-sectioned commercial ZnO varistor was probed laterally between the AFM tip and a bulk top electrode. Thus, in addition to the local impedance response at the AFM tip, non-local impedance contributions from any intervening grain boundaries between the tip and the bulk electrode are also probed.

Coupled SEM, AFM topography deflection, and AFM $Z_0$ images from a 50µm region of the ZnO varistor are shown in Fig. 12. The $Z_0$ image was acquired with a 100mV excitation signal under +5V DC bias at 1 kHz. Several distinct ZnO grains are visible in the images. The ZnO grains at the upper left of the image show purely ohmic behavior at a +5V DC bias. These grains are closest to the bulk top electrode, which was positioned approximately 30µm above and to the left of the image field of view.

Figure 12: a) SEM image of a 50µm region of a polished, cross-sectioned commercial ZnO varistor. b) AFM topography deflection image of the same 50µm region, acquired at 2Hz scan speed, 512 x 512 pixel resolution. c) Impedance modulus image of the same
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50µm region acquired according to the experimental configuration in Fig. 2a). Impedance modulus image data were acquired at 1 kHz with a 100 mV excitation signal and 5V DC bias. The bulk electrode for this measurement is located approximately 30µm above and to the left of the image field of view.

The highly nonlinear IV properties of ZnO varistors arise from double-Schottky like barriers formed at the grain boundaries of the material. Below a critical grain-boundary breakdown voltage (typically 3-4 volts), transport across the boundary is almost purely capacitive and the boundary is highly insulating. Above the critical voltage, however, transport across the grain boundary becomes ohmic.[38,39]

Fig. 13 shows a set of $Z_0$ and $\theta$ images for the same 50µm area at five different bias voltages ranging from 0V DC to +8V DC. (Measurements acquired at 1 kHz with a 100mV excitation.) Note how individual grain boundary barriers are shorted one by one during the DC bias voltage ramp, starting from the upper left with the grains closest to the electrode. This grain-by-grain cascade visibly demonstrates the highly nonlinear IV characteristics of the polycrystalline varistor. The first grains to exhibit ohmic transport characteristics do so at 3-4 V DC, indicating that they are removed by a single grain boundary from the top electrode. The other grains become ohmic between 5-8 V DC, indicating that they are probably separated by two grain boundaries from the top electrode. This result is reasonable given the varistor’s 40µm average grain size and the location of the top electrode 30µm above and to the left of the images.

**Figure 13:** Impedance modulus (top row) and impedance phase (bottom row) images measured as a function of DC bias for the same 50µm ZnO region documented in Fig. 12. From left to right, the images are acquired with increasing DC bias; 0V, 3V, 4V, 5V, 8V. All images acquired at 1 kHz with a 100 mV excitation signal. Note the grain-by-grain “cascade” with increasing DC bias as the grains become conductive, starting with the grains on the upper left closest to the bulk electrode.
Fig. 14 presents $Z_0$ and $\theta$ images as a function of measurement frequency for the same 50\textmu m area explored in Fig. 12 and 13. (Measurements acquired at +4V DC bias with a 100mV excitation.) Note the improved impedance contrast at lower frequency. This contrast improvement is expected based on an analysis of the RC-impedance behavior of the varistor grains. In single-frequency impedance imaging, careful choice of the imaging frequency based on the characteristic behavior of the analyzed system is necessary in order to achieve maximum impedance contrast. A theoretical treatment is intended for a later publication.

**Figure 14:** Impedance modulus (top row) and impedance phase (bottom row) images measured as a function of frequency for the same 50\textmu m ZnO region documented in Fig. 12 and 13. From left to right, the images are acquired with decreasing measurement frequency; 100kHz, 10kHz, 1kHz, 100Hz. All images were acquired with a 100 mV excitation signal and 4V DC bias. Note the improved impedance contrast at lower frequency.

Fig. 15 demonstrates the sub-micron resolution capabilities of the AFM impedance imaging technique with a series of “zoom-in” magnifications on a ZnO triple junction. The small triangular shaped region at the junction between the three ZnO grains (clearly visible in the 6\textmu m image) is a Bi$_2$O$_3$ second-phase inclusion. (Confirmed by EDAX analysis.) Bi$_2$O$_3$ is added to ZnO varistors to control the grain-boundary properties of the material. Excess Bi$_2$O$_3$ typically phase-segregates to the ZnO triple junctions. It is non-conductive.
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Figure 15: AFM topography deflection (top row) and impedance modulus (bottom row) images, increasing in magnification from left to right. (50µm, 15µm, and 6µm scan regions, respectively.) Impedance-modulus images are acquired at 1 kHz with a 100 mV excitation signal and 5V DC bias. The images “zoom” into a triple-junction region between 3 ZnO grains. The V-like intrusion between the 3 grains is a highly insulating Bi$_2$O$_3$ second phase inclusion. (Confirmed by EDX analysis.)

In addition to single-frequency impedance images, full impedance spectra can be acquired at specified locations on a sample. Fig. 16 compares impedance spectra acquired at several distinct locations on the varistor sample. Locations a) and b) are within ZnO grains, and show a transition from capacitive, blocked behavior at low DC bias to ohmic, conductive behavior at high DC bias. Location c) is inside a second phase Bi$_2$O$_3$ inclusion, and shows insulating behavior over the entire DC bias range.
Figure 16: Impedance spectra (Nyquist format) from various locations on the ZnO-sample surface. 

a) Impedance spectra vs. DC bias acquired at location a. Capacitive blocking behavior is seen for 0V and 3V applied DC bias. At 5V applied DC bias, an impedance loop develops.

b) Similar impedance behavior vs. DC bias is observed at location b on the sample surface.

c) At location c, capacitive behavior is observed at all levels of applied DC bias. Location c corresponds to a Bi$_2$O$_3$ second phase inclusion.

The AFM impedance technique may also be applied to studies of ionic materials and/or electrochemical systems. In this next section, we report localized impedance measurements on the protonated form of Nafion solid polymer electrolyte.

Following the experimental setup in Fig. 2c, a platinum coated AFM tip is used as a local probe of the proton (H$_3$O$^+$) density in a Nafion 117 membrane. (30 nm Pt sputtered over the standard conductive diamond AFM tip.) Hydrogen gas is provisioned to a sealed anode compartment underneath the electrolyte membrane sample, providing a continuous supply of protons into the membrane. (The anode is a standard polymer-electrolyte fuel cell catalyst-electrode, details given elsewhere.[40,41]) Applying a DC bias to the platinum-coated AFM tip (the bias is applied relative to the anode electrode, which is pseudo-reversible because of its much larger size) causes a Faradaic charge transfer reaction to occur, with protons from the membrane combining with oxygen from the air to produce water. Essentially, the Pt-coated AFM tip, in contact with the electrolyte membrane, becomes a tiny, moveable, fuel cell cathode. The kinetics of the cathode reaction will be proportional to the local concentration of protons in the membrane. Using
the AFM-impedance technique to probe this Faradaic charge transfer reaction permits the local activity of the electrolyte membrane to be visualized.

The impedance spectra in Fig. 17 confirm the ability of the Pt-coated AFM tip to act as a localized electrochemical probe. A Faradaic-like charge transfer loop is seen in the impedance response only if all of the following conditions are met:

1) A Pt-coated tip is used
2) H₂ gas is provisioned to the anode compartment
3) A cathodic DC bias is applied
4) The tip is in hard physical contact with the electrolyte membrane

Figure 17: Representative Nyquist impedance spectra for localized AFM impedance measurements on Nafion membrane. Impedance spectra are measured according to the experimental configuration in Fig. 2c) over the frequency range 100kHz to 100mHz with a 30 mV excitation signal. An impedance loop appears only when H₂ gas is provisioned to the anode, the AFM tip is in hard contact with the membrane, the AFM is coated with platinum, and a cathodic DC bias is applied to the tip. If any combination of the above conditions in not met, purely capacitive blocking behavior is observed instead. These observations suggest that the impedance loop behavior arises from a Faradaic charge transfer reaction occurring at the tip/electrolyte membrane interface.

Observation of this response only when all 4 conditions are met indicates that the loop most likely corresponds to a Faradaic reaction at the tip-electrolyte interface. This conclusion is supported by the behavior of the impedance loop with applied DC bias, as shown in Fig. 18. The loop shrinks with increasing DC bias, highly characteristic of a Faradaic charge-transfer reaction.
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Figure 18: Nyquist spectra of the Pt-tip/Nafion impedance response as a function of applied DC bias. Impedance spectra are measured according to the experimental configuration in Fig. 2c) over the frequency range 100kHz to 100mHz with a 30 mV excitation signal. H₂ gas is provisioned to the anode, the AFM tip is in hard contact with the membrane, and the AFM is coated with platinum. The impedance loop shrinks with increasing DC bias, characteristic of a Faradaic charge transfer process.

Translation of the AFM tip across the surface of the electrolyte permits spatially resolved “electrochemical” impedance images to be acquired, just as electrical impedance images were acquired for the gold patterns and the ZnO varistors. Fig. 19 shows sets of fixed-frequency AFM impedance images of a Nafion electrolyte membrane. These images were acquired at 1 Hz with a 30mV excitation signal, 0.4V DC cathodic bias (the bias favors the oxygen reduction reaction, thus decreasing the Faradaic charge transfer resistance and improving the signal to noise). The images compare the impedance response from a dry Nafion membrane (imaged under dry, 0% relative humidity, room temperature air) vs. the same area of the same membrane when hydrated (imaged under 30% relative humidity, room temperature air). The hydration level of the Nafion electrolyte significantly influences its solvated proton (H₃O⁺·nH₂O) concentration and conductivity. This is readily apparent from the AFM impedance images, which show a dramatic change in the impedance response (note change in the impedance scale). The corresponding topography images are not shown, but bear no relation to the impedance response. Membrane swelling and consequent dimensional expansion prohibited measurement of the membrane under still higher humidity levels.

It is well known that Nafion is not a homogeneous material, but instead consists of hydrophilic and hydrophobic phase-segregated regions. The apparent features seen in the Nafion impedance images of Fig. 19 may correspond to hydrophilic domains in the membrane. The apparent sizes of these domains (refer to the 1µm image) are on the order of several hundred nanometers. This is larger than the 40-100 nm domains visualized by
a SSPM study of dry Nafion recently published by Kiyoshi et al.[42] Kiyoshi and co-workers’ study looked at the variation in surface potential across a Nafion membrane. Several tens of high-surface potential spots were seen in a 10μm by 10μm scan of a Nafion membrane, and were attributed to hydrophilic water-containing regions in the Nafion electrolyte. The larger domain size in our results may be due to several factors, including drift, “smearing”, and the possible existence of a water meniscus at the tip/sample contact. The images in Fig. 19 were acquired in a vertical scan-mode. A possible vertical distortion or “smearing” effect can be seen in the 1μm images. We hypothesize that water from the hydrophilic domains on the Nafion surface might be captured on the tip as it steps from point to point, resulting in an extension, or “smearing” of the apparent hydrophilic domain sizes, especially in the scan direction. The formation of a water meniscus at the tip/sample junction would also serve to increase the overall apparent size of the hydrophilic Nafion domains. Nevertheless, these qualitative results show an overall decrease in impedance and an expansion of the low-impedance domains with increasing hydration, which are consistent with current knowledge on the behavior of Nafion.

**Figure 19:** Impedance modulus (top row) and impedance phase (bottom row) images of the Nafion electrolyte membrane as a function of humidity. The image sets on the left compare the impedance response under dry (0% relative humidity) vs. ambient (30% relative humidity) conditions for a 40μm area of the Nafion membrane. The image sets on the right compare the impedance response under dry vs. ambient humidity conditions for a 1μm area of the Nafion membrane. Images acquired at 1 Hz with a 30mV excitation signal, 0.4V DC cathodic bias. The hydration level of the Nafion electrolyte significantly influences its H$_3$O$^+$ concentration and ionic conductivity, as is readily apparent from the impedance images (note change in the impedance modulus scale for the left image set).
Progress

By improving fuel cell efficiency and lowering fuel cell costs, researchers can remove major remaining barriers towards widespread fuel cell implementation. These goals can be achieved by improving both catalyst activity, and by improving electrolyte conductivity. The triple phase boundary studies and AFM-impedance measurement system described in this report provide valuable research and development tools to further explore catalyst activity and electrolyte conductivity. Implementation of these new R&D tools over the next several years can help pave the way towards greater scientific understanding of catalyst and electrolyte phenomena, eventually leading to better fuel cell systems.

The combination of Atomic Force Microscopy with Impedance Spectroscopy provides unique insights into electrochemical behavior of a variety of materials important for fuel cell development. In particular, we have been able to measure the catalytic performance of PEM fuel cells comprised of one or a few nano-scale platinum particles. Our experimental configuration allows studying cathodic overvoltage, which represents a key bottleneck in improving fuel cell efficiency and power density. We are currently exploring AFM Impedance Spectroscopy measurements for the study of space charge phenomena in Solid Oxide Fuel Cell membranes. We expect to visualize spatial variations of oxygen ion conductivity and study the benefits of introducing linear lattice defects such as dislocations for enhancing ionic conductivity in electrolyte materials as well as and mixed electronic ionic conductors for electrodes.

Improvements in catalytic activity or increasing conductivity of electrode and electrolyte materials can substantially advance fuel cell power density and efficiency, a key performance metric for the practical use of fuel cells in cars.

Future Plans

The findings and techniques discussed in this report suggest many avenues for further research. Acknowledgement of the finite TPB width at Platinum/Nafion interfaces suggests new directions in catalyst layer design. Initial indications place the effective “TPB-width” on the order of many 10's to 100's of nanometers. This sets a target length scale for optimal catalyst layer nanostructures. It also suggests that novel planar-multilayered or intentionally patterned catalyst layers may prove effective.

The AFM impedance technique is ripe for application to many fields. To maximize the power and utility of the AFM impedance technique, further improvements in sensitivity, speed, and resolution should be investigated. Reduction of stray capacitance and other sources of spurious AC response can be achieved through careful tip design, thus allowing access to smaller RC time constants. The RC characteristics of the tip can be improved via selected area conductive patterning of the tip. Ideally, only the extreme end of the tip should be conductive, with only a small conductive pathway leading out to the measurement system. Further noise reduction and bandwidth improvement can be gained through tip shielding—for example with the development of innovative coaxial type tip geometries. Some of this exciting work is already ongoing by researchers around the world and by other members of our laboratory.[43,44]
Because the properties of an increasing number of materials depend strongly on nanoscale structure and processes, nano-scale characterization techniques such as AFM-impedance imaging are likely to be increasingly useful. Possible applications include solid electrolytes, semiconductors, solar cells, electro ceramics, coatings and corrosion research, and Li-ion battery and fuel cell systems. Localized AC impedance and transient potential techniques may be especially critical in the domain of electrochemical systems. Faradaic reactions, ionic transport and diffusion are best studied with transient techniques, making AFM impedance measurement extremely attractive for these applications.

Publications

References
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II.1.4 Nanoengineering of Hybrid Carbon Nanotube-Metal Nanocluster Composite Materials for Hydrogen Storage

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Introduction
The objective of this project is to develop optimized nanocomposite materials for high-density H₂ reversible storage applications. Specifically, carbon nanotube-catalyst nanoparticle composite materials with well-controlled nanotube size will be developed, that are optimized to satisfy the target fundamental characteristics for hydrogen storage. A systematic design and fabrication process will be followed that will permit not only controlled growth of carbon nanotubes but also incorporation of nanoparticles to decorate the nanotubes to catalyze H₂ adsorption and desorption processes.

Background
Nanomaterials have diverse tunable physical properties as a function of their size and shape due to strong quantum confinement effects and large surface/volume ratios. A single wall carbon nanotube (SWCNT) has the same structure as a roll of a single graphene sheet, and it has a nanometer-sized diameter ranging from 4 to over 100 Å. Due to their large surface areas with relatively small mass, SWCNTs have been considered as potential materials for high capacity hydrogen storage. Theoretically, they can store hydrogen up to 7.7 wt%, if every carbon atom in SWCNTs chemisorbs one hydrogen atom. In addition, the subsequent physisorption of hydrogen on the surfaces of hydrogenated SWCNTs can increase the capacity of hydrogen storage even further. In spite of the strong potential of SWCNTs, current experimental findings are not very promising mainly due to the lack of control in preparing SWCNTs as a hydrogen storage medium. It has recently been shown that the hydrogen-carbon nanotube interaction energy is a very sensitive function of the nanotube size, and a sample of a wide range of CNT sizes would have only a small fraction of the CNT surface suitable for hydrogen storage. There is currently much skepticism on carbon nanotube hydrogen storage due to early experimental mistakes, and therefore we are developing a rational basis for high capacity hydrogen storage materials through the systematic nano-materials approach we are taking in this project. The framework of nanomaterial design, fabrication and characterization that we are following to optimize catalyzed nanotubes for hydrogen storage is illustrated in Figure 1.
Results

We have initiated a systematic search process in material parameter space (particle composition and size) for optimized nanocomposite materials with high-density hydrogen reversible storage properties. The results to date from applying the four main thrusts of this approach are discussed below.

Nanoparticle Design and CNT Growth Modeling

Using the hierarchical multi-scale modeling approach described in Figure 2, we have investigated a rational simulation method to design metal nanoparticles for catalytic CNT growth applications. Figure 3 shows how metal nanoparticles are designed from continuum shape optimization to atomic structure relaxation to quantum simulation of chemical reactivity.
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To investigate the growth mechanisms of CNTs on metal nano-particle surfaces, we have investigated the hydrocarbon reaction on metal surfaces as illustrated in Figure 4 (left panel). Figure 4 (right panel) shows the results of CH₄ and C₂H₄ reactions on Ni(100), Ni(110) and Ni(111) surfaces. These results show that the reaction energies are \( \Delta E = -1.193 \sim -1.411 \, \text{eV/atom} \) for CH₄ and \( \Delta E = -2.221 \sim -2.439 \, \text{eV/atom} \) for C₂H₄ reactions, respectively. The difference in reaction energy indicates the efficiency of different hydrocarbons for CNT growth on Ni surfaces.

**Figure 4:** Modeling of CNT growth on metal surfaces

*Metal Catalyzed Multi-Wall Carbon Nanotubes*

It is clear from work at the National Renewable Energy Laboratory (NREL) and elsewhere that the content of nanostructured metal in carbon nanotube samples plays a critical role in the hydrogen storage capacity. For example, the storage capacity of nanotubes has been seen to greatly decrease after purification and removal of metal content. The form of the metal is also important, and the most effective form seems to be nanostructured metal particles in direct contact with the nanotube, such as the particles used in catalyzing nanotube growth. One interpretation of these results is that the metal is acting as a catalyst to assist in the hydrogen attachment process.
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Figure 5: Transmission electron microscope results from an as-received multi-walled carbon nanotube sample. Upper left shows the bright field image, upper right shows the dark field image with the diffracting regions appearing bright. Lower left is the diffraction pattern, which shows rings from C-graphite and bcc Fe with about a 3% lattice expansion. The bright regions in the dark field picture are associated with both these phases. The bottom right shows a high-resolution picture of a Fe catalyst particle at the tip of a nanotube.

In order to investigate the effect of metals on the hydrogen storage process we are conducting a study of controlled introduction of metal to carbon nanotube structures. Our approach uses the flexibility and versatility of ultra-high vacuum sputter deposition to introduce controlled amounts of metal directly onto the surface environment, which have an average diameter of 15 nm and average wall thickness of 4.2 nm. Nanotubes of this type typically have a hydrogen storage capacity of around 1.5 wt.%. The metal in these nanotubes is in the form of catalyst particles formed in-situ during their growth from a Fe precursor. As shown in Figure 5, the metal catalyst nanoparticles remain at the end of the nanotubes. Our transmission electron microscopy (TEM) investigation and our magnetization results (Figure 6) show that the catalyst particles are bcc Fe on carbon nanotubes.

Figure 5 shows the results from our TEM study of a multi-walled carbon nanotube (MWCNT) sample obtained from NREL. These nanotubes were placed in an ultrahigh vacuum deposition chamber, and one monolayer of Fe was deposited by sputter deposition. Post-deposition transmission electron microscopy was inconclusive about the state of this deposited Fe. We are currently investigating (in collaboration with NREL
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Figure 6: Magnetization results from an as-synthesized multi-walled carbon nanotube. Magnetization was measured in an ultra-sensitive alternating gradient magnetometer. The observed moment is from the Fe growth catalyst particles at the tip of the carbon nanotubes. The total mass of Fe for this sample was about 7 micrograms.

researchers) the change in hydrogen storage content associated with this controlled addition of metal. This initial investigation will be followed by a systematic study of the effects of the controlled addition of a variety of metals onto a variety of carbon nanostructures. We will work closely with the modelers on this team to design the ideal metal composition and morphology and investigate optimization of hydrogen storage capacity. These studies will be greatly assisted by availability of controlled structure nanotubes as our growth efforts progress, and will play a critical role in understanding and optimizing the hydrogen storage capacity of carbon nanostructures.

Single-Walled Carbon Nanotube Growth Control For Hydrogen Storage

One of the main ideas of our program is to control the size of SWCNTs to tune the H₂ storage capability. It is therefore critical to be able to synthesize bulk amounts of SWNTs with good structural control. To this end, we recently started a project to grow bulk quantities of SWCNTs using a Plasma Enhanced Chemical Vapor Deposition (PECVD) process we developed recently for growth on substrates. Growth is performed in a 4” remote PECVD system to produce high quality SWCNTs in bulk. Earlier experiments on SiO₂ substrates yielded tubes of fairly narrow diameter distribution that were nearly 90% semiconducting. To produce bulk catalyst, cobalt and iron acetate salts are dissolved in ethanol and loaded into a γ-type zeolite support or fumed silica. These supports afford small, uniform catalyst particles, and can be removed using HF after growth.

Our latest growth result is a PECVD tube material with a narrow diameter distribution, centered around 1nm. Raman data taken at 514 nm and 785 nm reveal tubes with a similar diameter distribution to HipCo (high pressure Co, Smalley’s process) and narrower than CoMoMAT (a material by the Resasco group known to have a narrow diameter distribution), and with evidence of a preponderance of semiconducting SWCNTs. From Figure 7, it appears that our PECVD SWCNTs exhibit a stronger Raman peak at around 260cm⁻¹ than the other materials, signaling that the nanotubes
mostly have diameters of around 1.2 nm.

We are currently optimizing the PECVD growth of SWCNTs by changing the catalyst support, metal compositions, loading percentages, temperature and plasma power. The growth parameter space will be fully explored to obtain SWCNTs with well-defined diameters.

![Raman Spectrum - 785nm Excitation of PECVD grown SWNTs.](image)

**Figure 7:** Raman Spectrum - 785nm Excitation of PECVD grown SWNTs.

*Spectroscopic Characterization of Hydrogen Storage*

One of the key issues regarding hydrogen storage in carbon nanotubes is the mechanism for hydrogen adsorption. Hydrogen can adsorb in either a molecular form or as atomic hydrogen. In the molecular form, hydrogen can either physisorb on the walls of the nanotubes or condense inside the tubes. In the second form, where dissociation takes place, strong C-H bonds will be formed. In the current project we intend to design properties of the carbon nanotubes where the covalent bond energetics is optimized for an overall hydrogen storage performance. It is essential in the initial phase of this project to identify the mechanism of hydrogen storage and under which conditions we form C-H bonds.

We are in the process of performing the first synchrotron radiation studies of hydrogen adsorption to carbon nanotubes. Beam time is scheduled at the Advanced Light Source in Berkeley during the first two weeks in August 2004. It is important to first characterize the changes in x-ray photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XAS) C1s spectra when atomic hydrogen is bonded to carbon atoms. The electronic structure of the substrate will undergo changes when the carbon atoms are rehybridized from sp2 to sp3 configurations. We are therefore currently building an atomic hydrogen source for dosing of hydrogen to the carbon nanotubes where we expect to obtain a reaction without the presence of a metallic catalyst for hydrogen dissociation. When we have a full understanding of the spectral changes due to C-H bond formation...
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we will also dose molecular hydrogen to follow the reactions with the nanotubes in the presence of a catalyst.

In parallel, we are currently preparing for Infrared Reflection Absorption Spectroscopy (IRAS) measurements of hydrogen coordination to the nanotubes. We expect to observe both C-H stretch vibrations from covalent bonded H atoms and H-H vibrations from strongly physisorbed molecular hydrogen. The initial experiments will be carried out with the atomic hydrogen source and later with molecular hydrogen. The first experiments using IRAS will be carried out during the month of September. When we can identify H coordination we can perform temperature program desorption (TPD) measurements following the evolution of molecular hydrogen in the gas phase with a mass spectrometer and also through the change in the intensity of the C-H stretch vibrations. These measurements will provide information from which we can derive the strength of the C-H bond.

In order to perform in situ measurements, we are constructing a cell where atmospheric pressures of hydrogen can be applied to allow both IRAS and XAS measurements. The intention is to see if other channels of hydrogen coordination will appear when larger pressures are applied. We can use isotopic substitutions of H\textsubscript{2} and D\textsubscript{2} to follow the exchange reaction at different temperatures, which will bring insights in the energetics of hydrogen storage.

**Progress**

During the first five months of this project, we have started to move forward with the framework of nanomaterial design, fabrication and characterization to optimize catalyzed nanotubes for hydrogen storage. Nanomaterial design is proceeding with metal catalyst optimization as well as a simulation study of CNT growth processes on metal surfaces. For controlled growth of CNTs, we are making fast progress using PECVD to attain CNT size control. Using the existing MWCNT samples, nanoscale characterizations are moving forward as well as identifying specific hydrogen signatures for spectroscopic characterization of chemically and physically stored hydrogen in nanotubes.

**Future Plans**

Our research project team has successfully initiated the individual research components of nanomaterial design, nanoparticle and nanotube fabrications, and characterization as well as linking them into a rational material development framework. During the rest of 2004, we will move forward with full multi-scale design of nanoparticles with two graduate students, one post doctorate, and two collaborators (Dr. Srivastava and Dr. Zhang). Dr. Zhang will visit Stanford during the summer to join the nanomaterial design efforts. We would like to purchase a highly sophisticated nanoparticle generator and hydrogen measurement equipment to prepare the initial batch of optimized catalyst nanoparticles for controlled CNT growth. These CNTs will be used for atomic hydrogen adsorption to calibrate the hydrogen capacity of the nanotubes as well as for characterizing the nature of stored hydrogen in CNT samples.
II.1.5 Hydrogen Effects on Climate, Stratospheric Ozone, and Air Pollution

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Introduction
The purpose of this project is to study the potential effects on global and regional climate, stratospheric ozone, and air pollution of replacing fossil-fuel based vehicles and electric power plants with those powered by hydrogen fuel cells, where the hydrogen is produced either from steam reforming of methane, coal gasification, or wind energy. The effects are being estimated with a three-dimensional numerical model of the atmosphere and ocean that is driven by emissions and that treats gases, aerosols, meteorology, clouds, radiation, and surface processes. An important part of the study is the development of emission scenarios for the model simulations.

Background
Over the last year, two important external papers have been published related to the effects of hydrogen on the atmosphere. In June, 2003, Tromp et al.\(^1\) examined the potential impact of increasing atmospheric hydrogen on stratospheric ozone. They suggested that the addition of hydrogen would increase the abundance of water vapor and cool the stratosphere, a process that would delay recovery of the ozone layer. The primary disadvantages of this paper were that they did not look at the effect of simultaneously reducing fossil-fuel emission, nor did they calculate the climate response of hydrogen itself. In October, 2003, Schultz et al.\(^2\) published a paper examining the effects of a hydrogen economy on tropospheric air chemistry and direct radiative forcing of gases. In their scenarios, they assumed that a reduction in anthropogenic emission would accompany an increase in hydrogen use. They calculated that NOx, CO, and OH would decrease in the global troposphere, and methane would increase upon switching to hydrogen. The increase in methane was estimated to increase global warming (although this was estimated, not calculated). The primary disadvantages of the study were that (1) it did not treat the effects of hydrogen on climate response (e.g., the model did not treat feedback to meteorology but rather simply examined the effects on chemistry and radiative forcing); (2) it did not examine the effects of switching to hydrogen on local or regional pollution (it examined only the large-scale effects); (3) it did not examine the effects of hydrogen on stratospheric ozone; (4) it did not treat aerosols or the effects of hydrogen on them; and (5) the emission scenarios were not resolved to the county or state level.

A few studies have also examined the economic benefits and drawbacks of different methods of producing hydrogen. A recently released DOE study\(^3\) investigated the infrastructure requirements to supply hydrogen to fuel cell vehicles from renewable
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resources. The study analyzed the economic and physical feasibility of producing enough hydrogen (10 quads) to supply a 2003-sized vehicle fleet in the year 2004 from renewable electricity sources, in particular, biomass, wind, solar photovoltaic, and geothermal. The study concluded that, among these sources, the most economically attractive and physically available renewable energy resource is wind power, potentially contributing 70.2% of the total energy required across the U.S., and at 40% lower cost than solar photovoltaic. The study also concluded that, in such a future scenario, Class 4 wind resources would be more highly utilized than Class 5 or Class 6 resources because of their proximity to population centers and consequent lower transmission costs. The greater feasibility of Wind Class 4 - generated hydrogen to a future fuel cell vehicle fleet underscores the importance of investigating this scenario for the GCEP study. Bauen et al. have also examined the importance of wind in creating renewable hydrogen for vehicles.

Results

Between January and May, 2004, several important goals of the project were addressed. An initial goal was to develop emission scenarios for the model simulations. This goal was met with respect to a scenario related to the conversion of the U.S. fleet of onroad vehicles to hydrogen fuel-cell vehicles where the hydrogen is obtained from steam-reforming of methane.

For this scenario, one model simulation will be run with the current fleet of U.S. onroad vehicles and a second simulation will be run with the fleet assuming emission associated with hydrogen fuel cells. Emission data for both the baseline and sensitivity simulation have now been prepared. For the baseline simulation, data for the U.S. were obtained from the U.S. National Emission Inventory, which considers 370,000 stack and fugitive sources, 250,000 area sources, and 1700 categories of onroad and nonroad vehicular sources (including motorcycles, passenger vehicles, trucks, recreational vehicles, construction vehicles, farm vehicles, industrial vehicles, etc.)

An emission inventory for the hydrogen scenario has also been prepared, by Dr. Whitney Colella. Figure 1 illustrates the primary mass, energy, and pollutant flows, as part of a Process Chain Analysis (PCA), in a realistic scenario devised for hydrogen fuel cell vehicles. In the scenario, hydrogen is derived from natural gas, which is extracted from gas fields, stored, chemically processed, and then transmitted through pipelines to distributed fuel processing units (following, up to this point, the same fuel cycle currently in place for gas turbine power plants and residential heating). The fuel processing units, situated in similar locations as gasoline refueling stations, convert natural gas to hydrogen via a combination of steam reforming and fuel oxidation. Purified hydrogen is then compressed for use onboard fuel cell vehicles.
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Figure 1. Process Chain Analysis of mass, energy, and pollutant flows in a scenario where hydrogen is obtained from natural gas.

The model simulations to be run require two primary sets of data: (1) the actual emission of gases and particle components associated with hydrogen fuel production and use, and (2) the corresponding reduction in emission associated with reducing fossil fuel use. The quantity of hydrogen-related emission is ultimately a function of the projected hydrogen consumption in on-road vehicles. Figure 2, derived here, shows the estimated
annual hydrogen fuel consumption by county in the United States resulting from the replacement of all on-road vehicles with hydrogen fuel-cell vehicles. The data for the figure were obtained by taking the number of miles driven in each U.S. county in 1999 from the U.S. National Emission Inventory, then converting the vehicle-miles travelled into energy requirements for propelling these vehicles (using the average fleet mileage of all on-road vehicles in the NEI’s 1999 database of 17.11 miles per gallon and an average gasoline vehicle efficiency of 16% based on Lower Heating Value (LHV) of the fuel), and converting the energy required for propelling the vehicles into hydrogen requirements (using an average hydrogen LHV vehicle efficiency of 53%).

From the hydrogen consumption information, estimates of leaked hydrogen, leaked natural gas, pollutants associated with the steam-reforming process, and pollutants associated with energy required to generate, transport, and compress hydrogen were derived. With respect to hydrogen leakage, we are considering three scenarios: 1%, 5%, and 10% leakage of all hydrogen consumed. Hydrogen leakage can occur during several of the processes in Figure 1. Instead of trying to quantify the actual leakage, which is not possible at this time, we will run scenarios that will provide results based on different assumed leakage rates so that the results can be interpolated once an actual leakage rate is known. With respect to natural gas leakage, we are using a standard estimated rate of 1.0% of additional natural gas consumption, which applies to incremental growth in the U.S. market for currently-available gas transport and processing technologies. With respect to gases emitted during steam-reforming of methane (carbon dioxide and water), we are calculating emission rates based on the stoichiometric ratio of products to reactants in the chemical reactions involved. Steam-reforming also requires energy to generate the steam. We are assuming such energy will come from oxidation of methane fuel. Energy is also needed for other processes. For example, in Figure 1, approximately 10% of the chemical energy (LHV) in the natural gas fuel is needed to produce hydrogen during the (1) exploration (0.7%), (2) production (5.6%), (3) storage and processing (1.0%), and (4) transmission (2.7%) of the gas. We are assuming that this energy is provided by electricity from the current mix of stationary power plants in the U.S. (approximately 51.7% coal, 19.8% nuclear, 15.9% natural gas, 7.2% hydroelectric, 2.8% oil, 2.0% nonhydro renewable, and 0.6% other fossil fuels in 2000). In later stages, energy is also required for hydrogen compression. These net energy inputs are also being derived from the current mix of stationary power plants in the U.S.
For the hydrogen scenario, the hydrogen fuel cycle must replace the gasoline fuel cycle, which is based on internal combustion engine vehicles. A gasoline fuel cycle is composed of similar process steps, including exploration, production, processing and refining, and fuel transport via trucks and tankers. Although the gasoline fuel cycle is more energy intensive in the production, refining and transmission stages than is the hydrogen fuel cycle, a first-cut analysis may assume similar levels of energy consumption requirements in the exploration through transmission stages.

Following its transmission stage, the hydrogen fuel cycle requires energy for fuel processing and hydrogen compression, and produces emissions in the form of natural gas leakage, hydrogen leakage, and products of steam-reforming of methane. The gasoline cycle, on the other hand, has fewer energy requirements but produces evaporative emissions of volatile organic compounds and combustion emissions of several pollutants (NOx, CO, HCs, CO, PM). In the scenario where gasoline emissions are replaced with hydrogen emissions, evaporative and combustion-related emissions in the U.S. National Emission Inventory will be eliminated.
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Two other tasks of the project in which progress was made during the first stage of this project were (a) developing scenarios for the case where hydrogen is obtained from wind energy and (b) improving the numerical model.

With respect to developing scenarios for wind, two important goals are (i) to locate where wind energy is prevalent and (ii) to locate where wind energy is viable. With these goals in mind Dr. Cristina Archer has been developing a detailed wind map of the United States. Data for the initial map were obtained only from surface and sounding information. Since January, she has obtained additional surface and sounding data to improve the mapping. In addition, she is now examining methods of coupling such data with satellite wind data and model results to fill in gaps where surface and sounding data are not available. Once the mapping is more complete, scenarios will be devised to determine where wind resources will most likely be developed to produce energy for hydrogen.

With respect to model improvements, Gerard Ketefian is improving a 3-D numerical ocean module that will be used in later stages of this project. The module is necessary for determining the long-term effect of changes in greenhouse gases and particles on climate. Since atmospheric perturbations to heating and cooling are diminished by energy diffusion to the deep ocean on a time scale of decades, accounting for the transport of energy to and within the deep ocean is an important goal. The model used for this project, GATOR-GCMOM, currently has a two-dimensional ocean module and treats energy diffusion to the deep ocean with fixed layers below the surface ocean, but energy is not transported in 3-D below the surface layer. As such, the implementation of a 3-D ocean module represents an improvement over what currently exists. It is estimated that the module will be ready for use in 4-8 months.

Model improvements have also been undertaken by M. Jacobson. Specifically, a numerical technique of solving nonequilibrium gas-aerosol transfer of acids and bases simultaneously and among multiple aerosol size bins has been improved. This technique is useful because it allows the solution of such transfer at long time steps with unconditional stability and without numerical oscillation. Growth of acids, such as sulfuric acid, nitric acid, hydrochloric acid, and carbonic acid, and growth of bases, such as ammonia, onto aerosol particles are important because it is a major mechanism of removing such acids from the gas phase, and the aerosols that form as a result have important effects on climate and air quality. The numerical scheme has been tested and will be used in the main model for the hydrogen scenarios.

Progress

Emission inventories have been prepared for a realistic hydrogen scenario (replacement of onroad vehicle fuels in the U.S. with hydrogen obtained from steam-reforming of methane). Emissions for other scenarios (including hydrogen production from wind) are also in progress. The numerical model to be used for the scenarios has been improved with respect to the treatment of nonequilibrium growth of acids and bases onto aerosol particles. A 3-D ocean module is also being improved.
Future Plans

The next stage of the project is to start running the first computer modeling scenario: a baseline simulation with the current fleet of U.S. onroad vehicles and a second simulation assuming the fleet is converted to vehicles using hydrogen fuel cells, where the hydrogen is obtained from steam-reforming of methane. Concurrently, the hydrogen scenarios will be expanded. Specifically, a scenario in which nonroad vehicles in the U.S. are converted to hydrogen fuel-cell vehicles, and a scenario in which fossil fuel power plants in the U.S. are converged to fuel-cell plants, will be developed. The wind scenario will also be expanded. Ocean model improvements will also continue.

Publications


References


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II.1.6 Solid-State NMR Studies of Oxide Ion Conducting Ceramics for Enhanced Fuel Cell Performance

Investigators
Jonathan Stebbins, Professor, Geological and Environmental Sciences; Fritz Prinz, Professor, Mechanical Engineering and Materials Science and Engineering; Namjun Kim, Post-doctoral Researcher; Cheng-Han Hsieh, Hong Huang, Graduate Researchers

Introduction
The purpose of this project is to develop new understanding of the atomic-scale structure and dynamics of oxide ion conducting ceramic materials that are at the heart of solid oxide fuel cells (“SOFC’s”), with the aim of more effectively optimizing their performance, lowering operating temperatures, size, and costs. Given the high efficiencies of fuel cells and their likely central role in future hydrogen-based fuel systems, SOFC’s may eventually play an important part in the GCEP mission of reducing total CO₂ emissions to the atmosphere.

An especially powerful experimental tool, which has received only limited application to such materials, is high-resolution, solid-state Nuclear Magnetic Resonance spectroscopy (NMR). We plan to use NMR to quantitatively characterize the structure of oxide ion conductors, in particular the nature of the order or disorder among dopant cations, that are difficult or impossible to obtain by other methods. We will study the effects of composition, temperature, and processing conditions on this structure, including exciting new thin film materials being developed in a related program by the group of Professor Fritz Prinz. We also plan to use the unique capability of NMR to detect the dynamics of ion motion in \textit{in situ}, high temperature experiments. We will relate both types of results to state-of-the-art electrical conductivity measurements, also in collaboration with the Prinz group. The combination of these approaches should lead to more fundamental understanding of the mechanism of ionic conduction in SOFC materials and hence provide new tools for engineering their properties.

This program is quite new, having started in mid-February with the hiring of an expert post-doc (Dr. Namjun Kim). This report will therefore focus on background material and then provide a summary of early program activities.

Background
Fuel cells, which directly convert the energy released by fuel oxidation to electricity, have been studied for decades as power sources that are cleaner and more efficient than conventional combustion-based systems. In most designs, the primary reaction involved is the oxidation of hydrogen by oxygen. In systems under development for use in the existing fossil fuel-based energy systems, the H₂ reactant is generally produced by “reforming” of gaseous hydrocarbons. In the short term, therefore, growing use of high-efficiency fuel cell-containing systems will contribute to net reductions in the rate of CO₂ emissions to the atmosphere primarily by lowering the amount of hydrocarbons that must be oxidized per unit of energy produced. In the longer term, however, movement towards a hydrogen-based fuel economy will be greatly facilitated by advanced fuel cell technology, which is ideally suited to the direct utilization of H₂.
Most common types of fuel cells are designed around gas-impermeable solid barriers that separate the H₂-rich fuel gas from the O₂-rich oxidant, but which allow rapid transfer of either H⁺ or O²⁻ by ionic conduction. The latter process is most common, using oxide anionic conducting electrolytes (most typically yttrium-stabilized zirconia or “YSZ”). The potential efficiencies of SOFC’s, especially when combined with cogeneration systems to fully utilize the byproduct heat, their modularity and unit size flexibility, and their environmental advantages (low SO₂, NOₓ, and particulate emissions), have led to major government and industry research and development efforts and the beginnings of installation of multi-megawatt commercial systems in distributed generation applications.

Typical SOFC’s must be operated at the relatively high temperatures (600 to 1000 °C) where electrolyte conductivity is sufficient to reduce resistive energy losses to acceptable values. Although high temperatures have the advantage of rapid redox reaction kinetics, and the ability to reform hydrocarbon fuels internally, they may limit the use of SOFC’s in applications that are critical to restructuring global energy systems, in particular to powering automobiles. (Note however that existing SOFC technologies are already being tested for powering long-range buses and trucks). Other types of fuel cells that operate at lower temperatures have thus been developed, for example those involving proton-conducting electrolyte membranes (“PEM” cells). Further advances in SOFC’s for some such applications will depend on increasing oxide membrane conductivity, by designing new materials and/or by developing new methods of fabricating much thinner electrolyte layers and integrating them into robust, miniaturizable fuel cell systems with fast warm-up times. The latter is one of the goals of another GCEP project, led by Professor Prinz.

The general principles of oxide ion conduction in ceramics have long been understood: O²⁻ ions diffuse through the crystal lattice at a rate that depends primarily on the concentration, distribution, and mobility of anion vacancies in the structure. Vacancies are most commonly introduced by creating solid solutions with cations having formal valences that are reduced from that of the host phase. For example, in zirconia (ZrO₂) “doped” with yttria (Y₂O₃, typically at the 9-10 mole % level), each mole of dopant introduces one mole of “missing” O²⁻. These vacancies provide abundant sites into which oxide ions can jump, enhancing conductivities by orders of magnitude.

Despite good understanding of the general principles of oxide ion conduction, a lack of information about atomic-scale structure and dynamics of these materials has hindered full development of predictive models of their properties. In particular, most oxide conductors are solid solutions that have complex but poorly-characterized degrees of cation and/or vacancy disorder that may vary with composition, temperature, and even the partial pressure of O₂. The extent and type of ordering can have major effects on conductivity. However, commonly-applied analytical techniques have been of limited utility in directly characterizing and quantifying such disorder. X-ray and neutron diffraction, for example, only reveal the structure averaged over long range, and can only hint at the energetically more significant short-range order/disorder.
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Methods of observing atomic-scale mechanisms of dynamics (the hopping from site to site that controls diffusivity and conductivity) are even more limited, and for the most part rely on modeling of bulk property data collected over ranges of temperature, composition, and external conditions. Information about preferred structural pathways for ion migration, about frequencies of ion exchange among locally different types of sites, and about mobility of populations of ions in energetically distinct sites can in general thus be only inferred. An experimental approach potentially capable of determining such mechanisms directly is thus highly desirable for a more accurate view of these critical details.

An example of this type of problem is shown in Figure 1, which illustrates two of many possible variations in the atomic-scale structure of a fuel cell electrolyte material, focusing on the differences in the distributions of the major and dopant cations around the oxide ions. These differences are likely to exert critical control over the properties of the material, but have been very difficult to directly characterize.

Over the last twenty years, solid state nuclear magnetic resonance (NMR) has

![Figure 1: Two-dimensional “cartoon” of possible atomic-scale structures of an oxide ion conducting ceramic such as yttrium-stabilized zirconia (YSZ). Two different states of cation disorder are illustrated, with the different types of oxide ion (red) coordination shells shown. The two states give measurably different distributions of oxygen coordinations, as shown by totals in lower part of figure.](image-url)
developed into a powerful new method for elucidating the short-range structure of disordered oxide materials. Even more uniquely, NMR can often directly sample ion dynamics at the microsecond to second time scales required to characterize diffusion in disordered crystalline systems.

NMR provides information primarily about local structure around isotopes of specific elements in crystalline, amorphous, or liquid materials. Spectra are thus primarily controlled by the number and spatial distribution (symmetry) of first and second atomic neighbors. In many cases it is this short- to intermediate-range structure that has the greatest energetic importance in controlling disorder and ion mobility. Among spectroscopic methods, NMR is unusual in that the strength of the observed signal in a properly designed experiment is directly proportional to the concentration of atoms in a given structural environment, providing an often unique approach to quantitatively measuring site occupancies and hence the ordering state.

The common (and structurally predominant) element in all of these materials is of course oxygen. However, the only NMR-active stable isotope of oxygen, $^{17}$O, has a natural abundance of only 0.035% and a moderately low resonant frequency (which contributes to lower sensitively and increased quadrupolar line broadening). Isotopic enrichment by up to $>1,000$ times is usually needed to observe high-quality spectra, especially where disorder and local site distortion produce relatively broad peaks. Such enrichment is not inexpensive, but is feasible. In recent years, applications of $^{17}$O NMR to the structure of disordered oxide materials has burgeoned with the development of synthesis methods, new high-resolution techniques (for example, “triple-quantum magic-angle spinning” or “3QMAS”), and correlations of observables with structural variables. In many cases, spectral sensitivity and resolution have been greatly enhanced by the availability of higher field NMR magnets (e.g. 14.1 and 18.8 Tesla, and even higher). Oxygen-17 NMR on oxide ion conducting ceramics has been demonstrated to be feasible and interesting, but applications have so far been limited. Because of the great potential of this approach for obtaining structural and dynamical information on a wide range of oxide ceramics, we have chosen to emphasize it in our planned research. For example, in at least some types of doped zirconia-based oxide ion conductors, we expect to be able to use this method to actually count the different types of oxygen sites as illustrated in Figure 1, providing for the first time a direct view of this critical aspect of the structure.

Two types of NMR methods can be used to elucidate diffusive time scale dynamics in solids. The approach that has been and continues to be most widely applicable is the measurement of spin-lattice relaxation times (“$T_1$”), which characterize the rate of transfer of nuclear spin energy to random thermal energy of the host material (“lattice”) after perturbation by NMR excitation. Because this transfer generally must be stimulated by fluctuations in the local magnetic field or electric field gradient at the Larmor frequency, $T_1$ measurements are sensitive to dynamics in the 10’s to 100’s of MHz range or at time scales of micro- to nanoseconds, which are often in the range of ion hopping frequencies in conductive solids at high temperature. Although such data can in principle be collected for any observable NMR signal on any nuclide, in practice it can be quite complex to relate such data to details of dynamics, as relaxation can be caused by local ion motions (e.g. the “rattling” of a cation in its “cage” of coordinating anions), by the motions of other ions in the structure, as well as by the through-going, site-to-site
hopping of greatest relevance to conductivity. Nonetheless, a number of studies spin-lattice relaxation of solid cationic conductors have proven to be useful.

A second approach has become more feasible with the improvements in the resolution of solid NMR spectra brought by “magic angle spinning” (where the sample is rapidly rotated at an angle of 54.7° with respect to the external field) and high magnetic fields (which reduce the quadrupolar effects that often broaden spectra for nuclides such as $^{17}$O). If NMR spectral peaks for different types of local structural environments can be resolved, then exchange of an ion among those sites can be detected when the exchange frequency becomes similar to the frequency separation of the peaks. In favorable cases, the exchange frequencies over a range in temperatures can be quantified by computer simulations of the resulting partially to fully averaged peak shapes. Because peak separations in typical spectra are on the order of about 100 Hz to 100,000 Hz, this approach can sample dynamics at much slower time scales than relaxation measurements (10’s of milliseconds to 10’s of microseconds) and thus can be used to study diffusion mechanisms at much lower temperatures. By using two-dimensional exchange spectroscopy, site exchange at even slower rates (on the order of seconds) can be detected. Very recently, the possibilities of using this approach for oxide ion conducting

Figure 2: Oxygen-17 NMR spectra of a bismuth vanadate oxide ion conductor (1) collected at the temperatures shown. At higher temperatures, the multiple peaks for oxygen in various sites in the vanadate layers merge together, indicating ion hopping among those sites only, thus helping to define the mechanism of conduction.
ceramics has been beautifully demonstrated for a series of bismuth vanadates and related materials, with high resolution 1-D and 2-D $^{17}\text{O}$ spectra collected up to 250 °C (Figure 2). Here, multiple peaks in the spectra, and the averaging among some of them that takes place even at this relatively low temperature, allowed site-specific exchange to be detected for the first time in such materials. The first author of this landmark study, Dr. Namjun Kim, has joined our program at Stanford to continue such studies and expand them into materials more applicable to fuel cell electrolyte membranes.

Results

We have spent the first several months of this project laying the groundwork for our planned studies. The lead post-doc, Namjun Kim has been hired. Two graduate students have been recruited: Cheng-Han Shieh is working closely with Dr. Kim and Professor Stebbins on beginning to synthesize zirconia-based ceramics and to become trained in NMR methods; Hong Huang is working with the group of Professor Prinz on thin film materials.

We have made good beginnings at several of the key aspects of the project. Design specifications have been completed and an order placed for a unique, state-of-the-art high temperature magic-angle spinning NMR probe, being built by Doty Scientific, Inc., and capable of in situ observations of oxide ion site exchange to temperatures as high as 700 °C. A special vacuum line system for exchanging $^{17}\text{O}_2$ gas into ceramic materials has been designed and largely completed, and an initial supply of this valuable gas has been purchased. Initial tests of sol-gel methods for the synthesis of homogeneous, nano-sized particles of doped zirconia have been made and methods are being refined; components for pressing samples into compact ceramic materials have been ordered or designed.

Progress

It is too early in this project to predict in detail its specific consequences for reduction in global CO$_2$ emissions. However, its most important overall goal is to provide the detailed, mechanistic understanding of fundamental processes in fuel cells that is needed to optimize their performance sufficiently to allow them to take their role as key elements in future hydrogen-based energy systems. If such systems do indeed become a major part of a global, reduced-CO$_2$ energy economy as is being explored by GCEP and many other research efforts, then the impact of our planned studies may be quite significant.

Future Plans

We plan to synthesize a number of different zirconia-based ceramic materials, selected both for their technological interest and the likelihood that they will yield NMR spectra with high information contents. For example, scandium-doped zirconia is a good candidate in both categories, and is thus a high priority. We are exploring several published methods of synthesis, the most promising of which relies on aqueous precursors to produce extremely fine-grained materials with homogeneous distributions of dopant cations. After high-temperature sintering (under a variety of conditions and thermal histories), we will exchange much of the isotopically normal oxygen in the samples with oxygen highly enriched in $^{17}\text{O}$ above its normal, 0.04% natural abundance, using in most cases a gas source and relying on the inherently rapid oxide ion diffusion of these materials to facilitate the exchange.
We will then carry out a number of different high-resolution solid-state NMR experiments on the materials, particularly emphasizing $^{17}$O spectra, which we expect to provide unique new information about the extent of order/disorder among dopant ions, whether or not defects and vacancies are clustered, and effects of composition and heat treatment on such structural details. As appropriate, we will observe other NMR-active nuclides as well, such as $^{89}$Y, $^{45}$Sc, and $^{25}$Mg. For “quadrupolar” nuclides, particularly $^{17}$O, we will employ advanced two-dimensional techniques including “multiple quantum” NMR to maximize spectral resolution, and, for the same reason, will collect data at very high external magnetic fields (14.1 and 18.8 Tesla, on “600 MHz” and “800 MHz” spectrometers). Quantitative analysis of these data should allow us to make new energetic models of cation and vacancy distributions, analogous to studies that we have made of highly disordered amorphous oxides (2-5). These results will be interpreted in light of electrical impedance spectroscopy made in collaboration with the group of Professor Prinz. Also working with that group, we will perform similar studies on thin film materials.

Somewhat later in the project we will begin in situ, high temperature NMR studies, again emphasizing $^{17}$O, to characterize the atomic-scale mechanisms of ionic transport. We will apply two approaches. In systems where we find multiple, well-resolved spectral peaks (e.g. Fig. 2), we expect to be able to observe exchange among sites directly, measure its average rate, and use this to test and constrain models of conductivity, as we have previously done on several cationic conducting oxide materials (6-8). In less well-resolved systems (for example, yttrium-stabilized zirconia), we will use measurements of “spin-lattice” relaxation times to elucidate ion transport. Again, impedance spectroscopy is planned on the same samples, to allow us to relate observed atomic-scale mechanisms to desired electrical engineering properties.

References

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II.2 Introduction to Renewable Energy

Research in the Renewables area seeks to develop technology which can be used to harvest solar, wind, geothermal and other forms of energy that are continuously replenished by existing geophysical processes at a rate exceeding the rate of extraction. In the long term, renewable energy has the potential to be carbon-neutral, and is therefore very appealing. GCEP currently has one project in solar energy conversion in its renewables portfolio, and will seek to add further projects in future solicitations.

Professor McGehee is developing nanostructured photovoltaic materials that could be deposited in reel-to-reel coating machines. This research will lead to devices that will efficiently split excitons and carry charge to electrodes, that will have improved packing of the molecules in the organic semiconductor to enhance its ability to carry charge, and that will have a modified organic-inorganic interface to prevent recombination of electrons and holes.
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II.2.1 Nanostructured Photovoltaic Cells

Investigators
Michael D. McGehee, Assistant Professor, Materials Science and Engineering; Yuxiang Liu, Vignesh Gowrishankar, Jarrett Dumond, Shawn Scully, Kevin Coakley, Graduate Researchers

Introduction
This project involves making efficient photovoltaic (PV) cells with semiconducting polymers that could be deposited in reel-to-reel coaters. Careful analysis and optimization of each process that occurs in bulk heterojunction PV cells will be carried out and devices based on ordered interpenetrating networks of organic and inorganic semiconductors will be created. Specifically, this research will lead to devices that will efficiently split excitons and carry charge to electrodes, that will have improved packing of the molecules in the organic semiconductor to enhance its ability to carry charge, and that will have a modified organic-inorganic interface to prevent recombination of electrons and holes. It is anticipated that charge recombination in the cells will be almost completely eliminated and energy conversion efficiencies in the range of 10-15% will be obtained.

Background
Currently the best commercially available PV cells are made of crystalline silicon and have an energy conversion efficiency of 12%. The cost of these cells is $3 per Watt of power generated under solar AM 1.5 conditions. These costs need to be reduced by an order of magnitude to around $0.3 per Watt for PV cells to be competitive with other energy generation systems and be manufactured on a large scale. A revolutionary breakthrough in reducing the costs of PV cells may be achieved if the semiconductor were deposited from solution onto large flexible substrates in reel-to-reel coating machines similar to those used to make food packaging. Manufacturing costs would be much lower because reel-to-reel coaters use very little energy and have an exceptionally high throughput. Installation costs would be lower because lightweight flexible PV cells could be handled more easily than heavy silicon panels. Since organic semiconductors, such as conjugated polymers, can be deposited from solution, they are very attractive for PV applications. Research on organic PV cells has shown that it is important to have two semiconductors with a large interfacial area so that photogenerated excitons can be split by electron transfer.[1-4] PV devices with interpenetrating networks of two semiconductors are known as bulk heterojunction cells.

The processes involved in operating a bulk heterojunction PV device are shown in Figure 1. To optimize performance of these cells, the desirable processes (1. light absorption, 2. exciton diffusion, 3. forward electron transfer, and 4. charge transport) should be maximized, while the undesirable recombination processes (5. geminate recombination and 6. back electron transfer) should be limited. This can be achieved by improving charge carrier mobility and slowing down the rate of back electron transfer so that photogenerated charge carriers can escape from the film before recombination occurs, while maintaining a thick enough film to allow most of the light to be absorbed.
Figure 1: A schematic diagram of the energy levels in an organic heterojunction photovoltaic cell and the electronic processes (defined in the text) that occur in one.

Results and Future Plans
Since the project began in January of 2004, we have focused our research on making inorganic semiconductor films with straight pores, improving exciton transport to organic-inorganic interfaces and increasing the charge carrier mobility of conjugated polymers confined to nanopores. These are important steps towards our long-term goal of enabling the reel-to-reel manufacturing of bulk heterojunction PV cells. We are currently preparing to submit these results for publication and when post them here when they have been published.
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Conference Presentations


References


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II.3 Introduction to Geologic CO₂ Sequestration

Fossil fuels currently dominate commercially supplied energy worldwide, and most estimates of energy use over the next 30 years suggest that use of fossil fuels will grow as the developing economies make greater use of energy. If that prediction is correct, then reduction of the amount of CO₂ emitted to the atmosphere will require that the CO₂ that results from combustion reactions be captured and stored. While many techniques are available for CO₂ separation, the cost of separation is still unacceptably high, and hence there is an opportunity for research in this area to lay the fundamental basis for more efficient separation methods. If the costs of separation can be reduced, then there is still the issue of where the CO₂ will be stored. This report deals with the possibility of storage in three geologic settings: oil and gas reservoirs, deep saline aquifers, and coalbeds. In each of these settings, sites will have to be selected that have appropriate geologic seals, efficient methods for flow predictions will be needed for process design and for permitting, and monitoring systems appropriate to various stages of a project will have to be designed. This report describes research to develop a suite of prediction tools appropriate to the flow settings and physical mechanisms that act and interact in the three geologic settings.

Oil reservoirs have considerable appeal as storage locations because they are known to have a geologic seal that trapped the hydrocarbons. Thus, as long as operations during oil production have not damaged that seal, the reservoir should be able to hold injected CO₂ indefinitely. Because oil (and also gas) reservoirs have known seals and because there is a regulatory structure that has experience in permitting gas-injection operations, existing oil fields are likely to be the first places that CO₂ sequestration is undertaken if it is to be done at large scale.

Storage of CO₂ can take place in zones in which CO₂ replaces reservoir oil or water. CO₂ is soluble in water, and it is about ten times more soluble in undisplaced oil. A separate CO₂-rich phase can also occupy significant pore volume. Movement of oil and gas in a reservoir is dominated by the pressure gradient created between injection and production wells and by the heterogeneity of the rocks. The viscosity of CO₂, a few hundredths of a centipoise over a wide range of pressures and typical reservoir temperatures, is low compared to most oils and any water present in the reservoir. The injected CO₂ invades high permeability flow paths as it makes its way to production wells. Accurate prediction of the timing of breakthrough of injected CO₂ at production wells and the amount of CO₂ produced with the oil requires detailed description of the permeability distribution in the reservoir. Those predictions are important because they forecast the amount of subsequent production, recompression, and recycling of CO₂ that is produced with oil.
CO₂ injection into gas reservoirs has been proposed but not yet been attempted. CO₂ could be used for pressure maintenance or for condensate vaporization, but the cost of purchasing CO₂ has so far prevented these applications in the absence of incentives for CO₂ storage. In fields that contain some condensate saturation, CO₂ can vaporize the light hydrocarbons that make up the condensate quite efficiently (see below), and it is even possible for CO₂ to develop multicontact miscibility with two-phase gas and condensate mixtures¹. If CO₂ sequestration were undertaken in a substantial way, gas reservoirs would be candidate storage locations, again with a known geologic seal capable of holding gas indefinitely.

Storage of CO₂ in a gas reservoir would have the advantage that all CO₂ that results from oxidation of CH₄ produced from the reservoir could be stored in the same reservoir, at the same temperature and pressure, with volume left over. One mole of CO₂ is produced for each mole of CH₄ oxidized, and the molar density of CO₂ is always larger than that of CH₄ at a given temperature and pressure. Figure 1 shows molar densities of CH₄ and CO₂ calculated with the Peng-Robinson equation of state² with volume translation³. The higher molar density of CO₂ means that the volume of CH₄ produced from a gas reservoir could be replaced by a mixture of N₂ and CO₂. In other words separation of all of the N₂ from a flue gas, for example, would not be required to match injection and withdrawal volumes, although there would be additional cost associated with compression of the N₂/CO₂ mixture over that for CO₂ alone. Figure 2 shows that a mixture of 60% N₂ and 40% CO₂ has approximately the same density as pure CH₄ at 50, 75, and 100°C.

![Figure 1: Molar density of CH₄ and CO₂.](image-url)
Oil and gas reservoirs are not uniformly distributed geographically, and there are many locations where anthropogenic CO$_2$ is generated that are not close to potential storage sites in oil or gas reservoirs. Deep formations that contain salt water are more widely distributed, however.

In this setting, injected CO$_2$ will also flow more easily through high permeability paths, but the flow will not be dominated by the pressure gradients imposed by injection and production wells. Gravity segregation caused by the difference in density of the injected CO$_2$ and brine will cause preferential flow at the top of the aquifer, though injection of the CO$_2$ well below the top of the aquifer can mitigate this gravity segregation to some extent. Aquifers with large volume, reasonable permeability and thickness, and good pressure communication over long distances will be most attractive, so that large volumes could be injected without raising aquifer pressure significantly. The injected CO$_2$ will dissolve, eventually, in the brine, and the resulting brine/CO$_2$ mixture will be slightly denser than the brine alone$^{4,5}$. Slow vertical flow of the denser brine will cause further dissolution, as fresh brine is brought in contact with the CO$_2$ phase. Trapping of a separate CO$_2$ phase by brine can also act to immobilize CO$_2$ as a residual phase$^5$. Estimates of the time scales for dissolution and the resulting vertical convection suggest that hundreds to thousands of years will be required to dissolve all the CO$_2$,$^{4,5}$ but by that time, much of the CO$_2$ will exist in a trapped residual phase$^5$. Relatively slow chemical reactions, depending on the chemical composition of the brine and the minerals present in the aquifer may then sequester some of the CO$_2$ as minerals$^6$.

In oil and gas reservoirs and aquifers, injected CO$_2$ occupies the pore space as a separate phase or is dissolved in water or oil. Deep, unmineable coal beds offer a different storage mechanism—the same mechanism that is the source of coal bed methane. Gases like CH$_4$ or CO$_2$ adsorb at high pressure on the surfaces of coal particles. They show what is typically observed: significantly more CO$_2$ adsorbs at a given
pressure and temperature on coal than does CH₄ or N₂. In addition, the hysteresis of the adsorption curves suggests that once the CO₂ is adsorbed, much of it will stay adsorbed even if the pressure is decreased at a later time.

Flow in coal beds will occur primarily in the fracture network (fractures in coal are known as cleats). Injected CO₂ will flow through the cleats, diffusing into matrix blocks, where replacements of adsorbed CH₄ by CO₂ will occur⁷. If that replacement occurs at reasonable rates, CO₂ can be used to enhance CH₄ recovery. This displacement process is similar to adsorption chromatography. Because CO₂ adsorbs more strongly than either CH₄ or N₂, it should be possible to use the coal bed to separate a mixture of N₂ and CO₂⁸, though at the cost of compression of the N₂ in addition to the CO₂ and the separation of N₂ from produced CH₄. There is evidence that coal permeability changes with the amount of adsorbed gas. As CH₄ is removed from coal, permeability typically increases, and as CO₂ adsorbs, permeability decreases. Thus, displacement processes in coal beds will involve a complex interplay of flow in the cleat system, changes in permeability, diffusion, and adsorption.

An important question, of course, is whether there is sufficient capacity available for storage of large quantities of CO₂ in the subsurface. Table I summarizes two sets of estimates of storage capacity in the subsurface. The ranges of the numbers are very large, an indication of the uncertainty in the estimates. Even so, the estimates are large enough to suggest that there is sufficient capacity to store a significant fraction of expected CO₂ emissions through 2030 and beyond. Current emissions are about 24 GtCO₂/yr (1 GtCO₂ = 1 billion metric tons of CO₂), and according to the estimates of the International Energy Agency¹⁰, are expected to rise to 38 GtCO₂/yr. If the rise in emission were roughly linear, then the total emissions would be about 1300 GtCO₂ for the period from 2000 to 2030. Thus, even given the uncertainty in the estimates, the capacity of geologic formations to store CO₂ appears to be sufficient to permit storage at significant scale.

<table>
<thead>
<tr>
<th>Storage Option</th>
<th>Parson &amp; Keith⁹</th>
<th>Gale¹⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil and gas reservoirs</td>
<td>740-1850</td>
<td>920</td>
</tr>
<tr>
<td>Deep saline aquifers</td>
<td>370-3700</td>
<td>400-10,000</td>
</tr>
<tr>
<td>Coal beds</td>
<td>370-1100</td>
<td>40</td>
</tr>
</tbody>
</table>

The existence of volumetric storage capacity is not sufficient, of course, to guarantee that CO₂ injection into the subsurface can be undertaken at scale. Many individual projects would be needed to accommodate the volumes of CO₂ that would have to be injected. For example, the Sleipner Project¹² is currently injecting about 10⁶ tCO₂/yr into a high permeability sandstone formation in the North Sea. One thousand similar projects would be required to store 1 GtCO₂/yr, and if the injected CO₂ had a density of 500 kg/m³ at reservoir conditions, the total injected volume would be about 34 million barrels per day. Thus, handling even 1 GtCO₂/yr, about 4% of current emissions, would require
substantial investment in separation capacity, infrastructure for transportation of the CO2, and wells and facilities for injection.

Identification of appropriate sites for geologic storage of CO2 will require work to establish that the injected CO2 will be retained in the subsurface. Research on the filling of oil and gas reservoirs indicates that stress changes associated with injection or depletion can affect the integrity of the geologic seals that contain the fluids. Accumulation of oil, gas, or CO2 can activate faults and cause leakage or can change the state of stress in such a way that leakage is less likely, so careful analysis will be required. More is likely to be known about the state of stress in oil and gas reservoirs than for aquifers or coal beds, so there will be a need for additional research in this area. Wellbores, which always penetrate the geologic seal, offer one potential pathway for leakage. Care will have to be taken to avoid sites and formations where there are abandoned wells that offer leak paths, and active wells will need to be well maintained. While operations at significant scale in enhanced oil recovery projects indicate that it is possible to conduct CO2 injection safely, careful attention will be needed to maintain safe operations in the many injection projects that will be required if geologic storage of CO2 is to take place at large scale.

Appropriate levels of monitoring of storage projects will also be needed. It is likely that more monitoring will be needed early in the life of a project than will be required later, but appropriate methods will need to be established for the various stages of a project. A variety of monitoring techniques have potential for use in CO2 storage projects. Seismic methods, which include time-lapse reflection or tomographic imaging and possibly passive seismic approaches can be used to detect subsurface migration and leaks. Gravity measurements and deformation methods such as synthetic aperture radar or tiltmeter measurements also have potential, though they will provide lower resolution indications of fluid movement.

Finally, use of geologic storage of CO2 at large scale will require establishing appropriate permitting processes for projects in deep saline aquifers, and perhaps for coal beds in some locations. It will be important in the design and permitting of projects to choose sites where the geologic seals provide long-term containment, to predict where the injected CO2 will migrate during injection, to monitor at appropriate levels where the injected CO2 has gone, and to understand the ultimate fate of the injected CO2. While a solid base of experience exists, there is much more to be done to design and optimize large-scale CO2 storage projects in geologic formations. In the remainder of this report, we consider three areas of research related to geologic storage of CO2: seal capacity, prediction of fluid movement, and monitoring.
II.3 Project Results: Geologic CO₂ Sequestration

II.3.1 Assessing Seal Capacity of Exploited Oil and Gas Reservoirs, Aquifers, and Coal Beds for Potential Use in CO₂ Sequestration

Investigators
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Background
In order for geologic CO₂ sequestration to be an effective tool in the stabilization of atmospheric CO₂ concentrations, a goal of sequestering about 3 Gt of carbon per year (~10 Gt CO₂/y) must be met by mid-century (based on current emissions predictions). Currently, pilot CO₂ sequestration projects such as Weyburn in Canada and Sleipner in the North Sea are sequestering on the order of 1 Mt CO₂/y. These pilot projects are important testing grounds for issues that will be faced as we move towards widespread sequestration implementation. It is important to look forward to the future of CO₂ sequestration and continue to evaluate the potential of as many large capacity repositories as possible.

Three options for geologic storage are unmineable coal seams, deep saline aquifers, and mature oil and gas fields. In the future, it will likely be necessary to exploit all of these possible options in order to make a significant impact on global atmospheric CO₂ concentrations. Coal seams offer the unique and attractive ability to store CO₂ by adsorbing it onto the coal surface. CO₂ injected for sequestration purposes can also be used to enhance the production of coal bed methane (CBM). Deep saline aquifers may provide the most capacity of the three storage options, but most are often poorly characterized as to their structure and physical properties. They are important sites because deep saline aquifers can be found in most areas with large numbers of CO₂ point sources, such as coal-burning power plants. Depleted oil and gas fields offer attractive benefits such as partially in-place infrastructures, extensive databases, and the possibilities for value-added benefits from enhanced oil recovery (EOR) and possibly enhanced gas recovery (EGR). Oil and gas fields have also contained large volumes of buoyant fluids for geologic periods of time, which means that at least in the past they had adequate seal integrity. The fact that hydrocarbon production is occurring suggests that the reservoir has a certain level of porosity and permeability as well as a reasonable capacity, which indicates that injection of CO₂ into the reservoir would be possible.

We are engaged in three parallel studies investigating geomechanics applied to seal integrity and CO₂ sequestration in geologic formations. These projects cover all three options for geologic CO₂ sequestration:

- **Unmineable Coal Seams:**
  - Powder River Basin (PRB)
  - Collaboration with Western Resources Project Foundation and Dr. Jonny Rutqvist at Lawrence Berkeley National Laboratory

- **Deep Saline Aquifers:**
  - Ohio River Valley CO₂ Storage Project
II.3 Project Results: Geologic CO\textsubscript{2} Sequestration

- Collaboration with Battelle, DOE, NETL, American Electric Power, BP, Schlumberger, Ohio Coal Development Office
- Depleted Oil & Gas Reservoirs:
  - Gulf of Mexico, South Eugene Island 330
  - Collaboration with ExxonMobil

\textit{CO\textsubscript{2} Sequestration and ECBM in Unmineable Coal Seams}

Coal seams are both a source of methane and a carbon-dioxide sink. For subbituminous coal like the ones in the Powder River Basin (Figure 3), the CO\textsubscript{2}/CH\textsubscript{4} ratio is approximately 10:1 (Figure 4), which indicates the great potential of the Powder River Basin to sequester this greenhouse gas. In addition, CO\textsubscript{2} can also be used to enhance the production of CH\textsubscript{4} from the coal seam since CO\textsubscript{2} has higher adsorption capacity than CH\textsubscript{4} in coal (see Figure 3). This means that the injection of CO\textsubscript{2} in coal beds works for sequestering CO\textsubscript{2} and also enhanced coal bed methane production (ECBM).

From our previous work in the Powder River Basin, we have found that it is typical during drilling and completion operations for the “water-enhancement” activities in the coal seams to result in hydraulic fracturing of the coal and possibly the adjacent strata thereby resulting in both excess CBM water production and inefficient depressurization of coals. We have been able to collect water-enhancement test data in coals to obtain the magnitude of the least principal stress in the coal seam. The preliminary data we have analyzed indicates that the hydrofracs are horizontal in some areas, such that vertical fracture growth is not a problem. However, vertical fracture growth does appear to occur in some places in the Powder River Basin. We are investigating the idea of using the hydrofracs that have been produced in the coals as a more effective path to inject CO\textsubscript{2} for sequestration and ECBM.

\textit{CO\textsubscript{2} Sequestration in Deep Saline Aquifers}

Several sequestration projects are looking at the deep saline aquifers in the Ohio River Valley as potential sites for CO\textsubscript{2} sequestration because of the large number of CO\textsubscript{2} point sources located in the Midwest. The Ohio River Valley CO\textsubscript{2} Storage Project is unique because it is a field investigation located on the site of the coal-burning Mountaineer Power Plant (Figure 5). Much of the field data needed to characterize the site has already been collected. A 2-D seismic survey through the site was collected in July of 2003. A 9190 ft well was drilled from May through July of 2003. The well was logged with a full suite of geophysical tools, including a Formation MicroImager (FMI) tool. Extensive core and brine sampling was also done. Pressure tests to determine the magnitude of the least principal stress are currently being performed in the well. All of this data is being analyzed to characterize the aquifer and the caprock for their CO\textsubscript{2} sequestration potential.
II.3 Project Results: Geologic CO₂ Sequestration

**Figure 3:** Topographic relief map of the Powder River Basin in Montana and Wyoming. The red dots cover the CBM development area. An existing CO₂ pipeline runs towards the southwest boundary of the basin, and there is a possibility that this could be extended into the PRB in the future.

**Figure 4:** Sorption capacity with respect to Coal Rank. The replacement ratio of CO₂-to-CH₄ is highest for low rank coals, e.g. sub bituminous coals (Bustin in Reeves¹⁸, 2003). The coal found in the Powder River
II.3  Project Results: Geologic CO$_2$ Sequestration

Basin is sub bituminous, making it a great candidate for CO$_2$ sequestration.

Figure 5: Location of the Mountaineer Power Plant, New Haven, WV. The pilot well (bottom left) for the Ohio River Valley CO$_2$ Storage Project was drilled on site at the power plant during the summer of 2003 (figures from Gupta$^{19}$).

CO$_2$ Sequestration in Depleted Oil and Gas Fields

Depleted oil and gas fields seem to be the natural choice for the first large-scale CO$_2$ sequestration operations. Currently, one of the largest CO$_2$ sequestration projects in an oil and gas field is taking place in the Weyburn field in the Williston Basin of Saskatchewan, Canada. The project combines CO$_2$ sequestration with EOR operations to store about one million tons of CO$_2$ per year. This is an extremely small fraction of the amount of CO$_2$ that must be sequestered to make a significant impact on stabilizing atmospheric CO$_2$ concentrations.

We are beginning to examine the sequestration potential of fields in the Gulf of Mexico by developing a workflow for assessing reservoir suitability for sequestration. There are a number of factors that make the Gulf of Mexico an appropriate site for developing a regional workflow. Extensive datasets are available that are crucial in building a comprehensive picture of the potential storage sites. The current petroleum industry infrastructure and the number of CO$_2$ sources near the Gulf Coast are integral steppingstones in the building of a complete CO$_2$ sequestration infrastructure (Figure 6).
II.3 Project Results: Geologic CO₂ Sequestration

There is also significant capacity for storage in the region as well as potential for value-added benefits from CO₂ EOR.

![Map of the U.S. Gulf Coast and Gulf of Mexico and some of the existing infrastructure in the region. Oil pipelines are in green, gas pipelines in red, and onshore pipelines in gray. The black figures are possible sources where anthropogenic CO₂ that could be captured and separated for sequestered in the Gulf of Mexico. In yellow is the location of our case study site, South Eugene Island Block 330.]

**Figure 6:** Map of the U.S. Gulf Coast and Gulf of Mexico and some of the existing infrastructure in the region\(^{20}\). Oil pipelines are in green, gas pipelines in red, and onshore pipelines in gray. The black figures are possible sources where anthropogenic CO₂ that could be captured and separated for sequestered in the Gulf of Mexico. In yellow is the location of our case study site, South Eugene Island Block 330.

**Results**

*Powder River Basin*

The first step in studying CO₂ sequestration coupled with ECBM in the unmineable coal seams of the Powder River Basin is mapping out areas where horizontal hydrofractures occur rather than vertical ones. Hydrofracs open horizontally when the least principal stress is the vertical stress (Sᵥ). The magnitude of the least principal stress is determined by pressure tests like the water-enhancement tests. We can calculate Sᵥ by integrating over the density log. If these two values are the same, horizontal hydrofracs can occur when the fluid pressures exceed the magnitude of the least principal stress.

Our next step is to run simulations of various injection scenarios. As shown in Figure 7, we intend to use stacked hydrofracs in the coal to inject CO₂ and produce CH₄. Specifically, we will investigate the efficiency of producing a hydrofrac towards the bottom of a coal seam where CO₂ would be injected, and a hydrofrac in the upper part of the coal seam from which CH₄ and water would be produced. The simulations have the following objectives:
II.3 Project Results: Geologic CO₂ Sequestration

- Examine multiphase flow characteristics of CO₂-H₂O-CH₄ system
- Test for hydrofrac spacing, thickness of coal seam, spacing of wells
- Investigate rates and volumes of sequestered CO₂ and produced CH₄

We also expect to find alternative ways of sequestering CO₂ in a specific setting like the PRB, which could take advantage of existing wells and hydrofracs during the injection of CO₂ into the coal.

![Figure 7: Schematic of suggested ECBM configuration. CO₂ is injected into the deeper horizontal hydrofrac. As the CO₂ front moves through the coal and is preferentially adsorbed, it displaces the methane. The free methane is then produced from a shallower horizontal hydrofrac.](image)

To do these simulations, we have been collaborating with Dr. Jonny Rutqvist from the Lawrence Berkeley National Lab. The computer code we are using is TOUGH2 with the CBM module added to it. TOUGH2 is a numerical simulator for nonisothermal flows of multicomponent, multiphase fluids in one-, two-, and three-dimensional porous and fractured media (Pruess et al.²¹). Modifications were made to one of the original modules of TOUGH2 to be able to apply it to ECBM simulations (Webb²²). The extended Langmuir isotherm for sorbing gases, including the change in porosity associated with the sorbed gas mass, has been included in the new ECBM module. We have started to build our code by creating meshes that would represent the structure that we want to study (described above, Figure 7) and during the test simulations, we are feeding the code real data.

**Ohio River Valley CO₂ Storage Project**

We are developing a comprehensive geomechanical model of the Ohio River Valley CO₂ Storage Project site. This is an integral step in the complete characterization of a potential CO₂ storage site that provides a good indication as to the suitability of these aquifers for long-term storage of anthropogenic CO₂. In particular, we are examining the
state of stress and fracture characteristics in the Rose Run aquifer as well as the layers adjacent to this formation. We have used the FMI log to pick the drilling-induced tensile fractures along the wellbore (Figure 8). These propagate in the direction of greatest horizontal stress, $S_{H\text{max}}$. The minimum horizontal stress, $S_{h\text{min}}$, is oriented $90^\circ$ from $S_{H\text{max}}$. From the drilling-induced tensile fractures, we have determined that $S_{H\text{max}}$ is oriented N47°E, and $S_{h\text{min}}$ is oriented N43°W (Figure 8). This is consistent with the regional stress. The presence of en echelon tensile fractures in the near-vertical wellbore indicates localized stress perturbations exist (Figure 8). The next steps in this study are to compile a pore-pressure profile of the well, the results of ongoing mini-frac tests to determine the magnitude of $S_{h\text{min}}$, and to integrate over the density log to get the vertical stress. Using this information, we can constrain the magnitude of $S_{H\text{max}}$ to complete our geomechanical model of the site. We have also used the FMI data to pick natural fractures that cross the wellbore.

We plan to use our geomechanical model and fracture characterization to determine the distribution and orientation of hydraulically conductive fractures within the aquifer and the effectiveness of adjacent layers to act as seals against the vertical migration of the injected CO₂. By assessing the magnitude of the least principal stress in the Rose Run aquifer, we will determine the injection pressure at which hydraulic fracturing will occur as well as the direction of the hydraulic fracture propagation. This is fundamental in the development of a safe and effective injection plan. We will also determine the maximum fluid pressures that can be maintained in the formations (i.e., their dynamic capacity) without resulting in frictional failure and leakage through hydraulically active fractures.

**Gulf of Mexico**

It is imperative to approach any assessment of CO₂ storage potential in the Gulf of Mexico from a geomechanical perspective. Many of the trapping mechanisms in the region depend on fault seal. So it is necessary to determine the initial state of the trapping and sealing mechanisms, examine the effect of production on the seal, and predict changes associated with CO₂ injection and storage (Figure 9). A complete geomechanical model is important in assessing the reservoir and seal conditions throughout the lifetime of the reservoir. We are using South Eugene Island Block 330 (SEI 330) as a case study site to develop and test a geomechanical workflow for assessing CO₂ sequestration potential in the Gulf of Mexico.

South Eugene Island Block 330 is located offshore of Louisiana about 270 km southwest of New Orleans. The field is part of a salt-withdrawal, plio-pleistocene mini-basin. Most of the reservoirs in the field are in the hanging wall of the major basin-bounding normal growth fault. Hydrocarbons are trapped by rollover anticlines created during salt-withdrawal related faulting. It is a mature field that was discovered in 1971 and began production in 1972. An extensive dataset exists for the field, including a recent 3D seismic survey, numerous well logs, bottom-hole pressure readings, and pressure tests (leak-off tests and formation integrity tests).
II.3 Project Results: Geologic CO₂ Sequestration

Figure 8: Drilling-induced tensile fractures from the AEP#1 well drilled on site at the Mountaineer Power Plant in New Haven, WV. A) FMI image showing en echelon drilling-induced tensile fractures. The color scale is conductivity. The green line shows the orientation of caliper 1; the pink lines are picks of the individual fractures. B) A plot of azimuth vs. length of the tensile fractures picked from 6400 ft to 9100 ft. The mean azimuth is 47°, so we estimate that the orientation of S\text{Hmax} is N47°E.

Figure 9: The strategy for building a geomechanical sequestration site assessment is to integrate data from the three stages in the lifetime of a field.
Dynamic constraints on hydrocarbon fill are of interest when looking at this field as a possible site for CO₂ sequestration. Dynamically controlled reservoirs are pressure-limited rather than volume-limited, making it more difficult to determine the capacity of the reservoir for CO₂ storage. Examples of dynamic controls on hydrocarbon fill are capillary entry pressure of the caprock, hydraulic fracture limit (equal to the magnitude of the least principal stress), and dynamic fault-slip limit (equal to a critical pore pressure based on the state of stress and Coulomb failure criterion). When any one of these pressure limits is reached at the top of a reservoir, the caprock cannot support any additional hydrocarbons. If additional hydrocarbons enter the system, the dynamic control acts to release the fluids, through capillary entry, hydraulic fracturing or dynamic fault slip, which decreases the buoyant pressure on the caprock (Figure 10). This presents a unique problem when injecting CO₂ into dynamically constrained reservoirs. Because the density of CO₂ at normal reservoir conditions is about 500-700 kg/m³ depending on temperature-and-pressure conditions, an oil reservoir can hold a smaller volume of CO₂ than oil, but a gas reservoir can support a larger volume of CO₂ than gas (Figure 10). In reality, the fluids in a reservoir undergoing sequestration operations will be a complex, time-dependent mixture of oil, gas, and CO₂. Therefore, it is important to fully understand the initial controls limiting hydrocarbons in the reservoir prior to production and have production history data to be able to estimate the capacity of reservoir to store CO₂.

**Figure 10**: Effect of buoyant fluids on reservoir capacity in the presence of pressure-limited seals. A) Modified from Finkbeiner et al.\textsuperscript{23}, at T₀ there are no hydrocarbons in the reservoir, and the pressure at the cap rock falls along the pressure gradient of water in the aquifer. As the reservoir fills through time from T₀ to T₃, the pressure at the top of the reservoir increases, falling along the hydrocarbon pressure gradient. When the buoyancy force on the cap rock equals the pressure limit, the seal cannot support any additional...
hydrocarbons. B) The different buoyancies of oil, CO₂, and gas affect the volumes of these fluids that can be sustained by a pressure-limited seals.

A study by Finkbeiner et al.²³ shows that dynamic controls on hydrocarbon fill exist in some of the reservoirs in South Eugene Island 330. One example of a dynamically controlled reservoir is the OI-1 sand in Fault Block A. Figure 10, which is modified from Finkbeiner et al.²³, is a pressure vs. depth plot that illustrates the dynamic fault-slip limit is acting as a control on the seal capacity of the OI-1 sand in Fault Block A. The blue line is hydrostatic pressure, and the black line is the overburden pressure. The green dashed line is the hydraulic fracture limit or least horizontal stress, interpolated from leak-off tests and formation integrity tests. The yellow box is the dynamic slip limit calculated from the overburden stress and the least horizontal stress over a range of coefficients of friction between 0.3 and 0.6. The oil columns are shown in green, and the gas columns in red. The pressure at the top of the oil leg reaches the dynamic fault slip limit, suggesting that this reservoir is controlled by dynamic fault slip. However, other shallower sands in the same fault block are clearly not limited by the dynamic fault slip or hydraulic fracture limit.

**Figure 11:** Pressure vs. depth plot of SEI 330 Fault Block A. The oil column in the OI-1 sand appears to be controlled by the dynamic slip limit, while the other shallower sands are not limited by that dynamic control. See text for more explanation. We are developing
II.3 Project Results: Geologic CO₂ Sequestration

a geomechanical workflow in the context of the SEI 330 field (Figure 12). We have chosen to study this field in more detail because previous studies have brought a number of interesting yet unresolved questions to light about topics such as the relationships between fault blocks, fluid migration, sources of overpressure and controls on hydrocarbon column heights (Alexander and Flemings; Alexander and Handschy; Gordon and Flemings; Losh et al.; Stump and Flemings; Finkbeiner et al.; Losh et al., and others). Many of these studies are based on the structure maps generated by Pennzoil over a decade ago. Currently, ExxonMobil is creating structure maps based on a newer 3D survey using the advanced interpretation tools now available. We will reevaluate SEI 330 based on these new structural interpretations and see if this affects the interpretations that were made in the previous studies.

Figure 12: Initial draft of the Workflow for Assessing Reservoir Suitability for CO₂ Sequestration in the Gulf of Mexico.
II.3.2 Rapid Prediction of CO2 Movement in Aquifers, Coal Beds, and Oil and Gas Reservoirs

Investigators
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Background
Considerable effort has been devoted to the development of reservoir simulation tools for the oil industry, and there are high-quality simulators available that handle effectively many of the flow problems appropriate to oil and gas reservoirs. One area where simulator development is continuing, however, is in the simulation of processes in which multiple components transfer between whatever phases are present in the porous medium. Injection of CO2 into geologic reservoirs inevitably involves such component transfers, as the injected CO2 dissolves in any water or oil present, as hydrocarbons transfer to the relatively dense CO2-rich phase, or as CO2, methane, and possibly N2 adsorb and desorb in coal.

Because the most important physical mechanisms of storage differ for the three geologic systems, it is appropriate to consider the current state of predictive models for each setting. Compositional simulation tools are best developed for oil and gas reservoir settings, for which several fully capable finite-difference compositional simulators are available. ECLIPSE 300 and GEM are examples. These codes use an equation of state to represent equilibrium partitioning of components between oil and gas phases, and they handle the effects of capillary pressure and gravity well. The principle limitations of these simulation tools are computation speed and the adverse effects of numerical dispersion on computed composition path. For aquifer and coalbed settings there are also several simulation tools available. The capabilities of some of them are reviewed in the paragraphs that follow.

TOUGH2 is a numerical simulator for non-isothermal flows of multicomponent, multiphase fluids in one-, two-, and three-dimensional porous and fractured media. TOUGH2 was originally developed for geothermal reservoir engineering, nuclear waste disposal and hydrology. There are several simulators in the TOUGH2 family that include physical mechanisms appropriate to CO2 sequestration in aquifers, including TOUGHREACT/ECO2 (includes transport of aqueous liquid and vapor phases by advection, chemical reactions for dissolved species and minerals, and molecular diffusion in both liquid and gas phases), ChemTOUGH (implicit formulation that allows larger time steps but requires substantially more memory), and TOUGH2-FLAC3D (couples TOUGH2/ECO2 with FLAC3D which models rock and soil mechanics). This family of simulators generally makes use of the equilibrium assumption: components equilibrate rapidly among whatever phases are present. An exception is made for mineral dissolution and precipitation, which can be modeled as in local equilibrium or subject to a kinetic model.
NUFT\textsuperscript{30} is an integrated software package containing five application specific modules, for the simulation of multiphase and multicomponent flow and reactive transport within a wide range of subsurface environments. The code can model multiphase advection, diffusion, dispersion, relative permeability, and kinetically controlled fluid-mineral reactions. The feedback between transport and geochemical reactions can be modeled by dependence of the permeability on porosity changes due to reactions. PVT properties of CO$_2$ and water are calculated from equation of state formulations. The SUPCRT92 software package is used for calculation of fluid mineral equilibria\textsuperscript{31}. It provides standard state thermodynamic data and equilibrium constants for a wide range of minerals, gases, and aqueous species over a wide range of temperatures and pressures.

FLOTRAN\textsuperscript{32} describes coupled thermal-hydrologic-chemical processes in variably saturated, nonisothermal, porous media in three dimensions. FLOTRAN describes systems involving two-phase fluid flow and multicomponent reactive chemical transport involving aqueous, gaseous, and mineral species. FLOTRAN includes separate modules that handle the mass and energy transport and the reactive transport. FLOW solves the mass conservation equations for water and gas and energy. TRANS solves mass conservation equations for a multicomponent geochemical system. Effects of capillary, gravity, and viscous forces are included, as are energy transport by convection and conduction. The equilibrium assumption is made for chemical reactions, with kinetic representations available for mineral dissolution and reaction. Changes in porosity and permeability can be represented.

STOMP\textsuperscript{33} is a computer model for simulating subsurface flow and transport. Solute transport, radioactive decay, and first-order chemical reactions modeled, following the solution of the coupled flow equations. Reactions and transport are coupled to the flow by accounting for changes in host rock porosity and permeability. An equation of state for CO$_2$ is included that handles a wide range of temperatures and pressures to 800 bars. Options appropriate to sequestration include H$_2$O-CO$_2$-NaCl, H$_2$O-CO$_2$-NaCl-Energy, H$_2$O-CO$_2$-CH$_4$-NaCl, and H$_2$O-CO$_2$-CH$_4$-NaCl-Energy. Extension to account for other geochemical reactions is planned.

The UTCOMP simulator is a three-dimensional, isothermal, equation-of-state compositional simulator\textsuperscript{34}. The simulator can be used to study the effects of physical dispersion, gravity, reservoir heterogeneity, phase behavior, fingering, relative permeability and capillary pressure effects including capillary number, and reactive and partitioning tracers. A maximum of four phases is permitted to co-exist, including one aqueous phase and three hydrocarbon phases. Local thermodynamic equilibrium between hydrocarbon phases is assumed with the exception of rate-limited mass transfer of surfactant between phases, rate-limited mass transfer of hydrocarbons into a flowing gas phase and reactive tracers. UTCOMP was written to simulate enhanced oil recovery, and several modifications are needed in order to simulate CO$_2$ sequestration. For CO$_2$ injection into aquifers, phase 2 was used for the aqueous phase, and phase 3 was the gas phase (supercritical CO$_2$ plus some H$_2$O as a dense fluid phase). Phase equilibrium in the binary CO$_2$-H$_2$O mixtures in each grid block is calculated using the Peng-Robinson
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equation of state. The effect of salinity on the solubility of CO$_2$ in brine is modeled by adjusting the binary interaction coefficients in the Peng-Robinson equation. Henry's law is used to model the solubility of CO$_2$ in water, including a correction for salinity of the brine.

Coalbed methane (CBM) simulators also model physical mechanisms thought to be important in CBE recovery and CO$_2$ storage processes: the dual porosity structure of the coal bed, adsorption/desorption of CH$_4$ at the coal surface, coal matrix shrinkage due to CH$_4$ desorption, and diffusion of gas from the matrix to the fracture system. Additional physical mechanisms that may play a role in CO$_2$ storage on coalbeds include: coal matrix swelling due to CO$_2$ adsorption onto the coal surface, mixed gas adsorption, and diffusion of multiple gas components.

Enhanced CBM simulators that are applicable to CO$_2$ storage can be divided into two groups: those that use a compositional framework, and those that adopt a black oil framework. In the compositional framework, fluid properties are rigorously modeled based on an equation of state. In the black oil framework, fluid properties are supplied by lookup tables obtained through laboratory work or correlations.

**Compositional Framework**

PSU-COALCOMP$^{35}$ is a compositional, dual porosity coal bed methane simulator that accounts for multi-component sorption and transport phenomena. Multicomponent sorption is modeled via an ideal adsorbed solution theory and the Peng-Robinson equation of state. Mass transfer between the matrix and fracture system is defined via a sorption time constant, a lumped parameter that incorporates diffusion time, rate or sorption/desorption and cleat spacing of the coal.

GCOMP a simulator that assumes instantaneous diffusion between the matrix and the fracture systems, allowing reduction of the system to a single porosity system$^{36}$. Mixed gas adsorption is modeled via an extended Langmuir model. In this approach, the concentration of each gas component is a function of its partial pressure. Geomechanical effects on permeability and porosity are modeled, as is coal matrix shrinkage and swelling due to adsorption/desorption of gases on the coal surface.

SIMED II is a two-phase multicomponent single or dual porosity coal bed reservoir simulator$^{37}$. The Peng-Robinson equation of state is used to calculate fluid properties. Water phase properties are evaluated internally. Multiphase gas adsorption can be modeled via an extended Langmuir isotherm or an ideal adsorbed solution model. Stress-dependent permeability and porosity can be accounted for through a choice of one of five models. SIMED II also accounts for geomechanical effects associated with injection. A dynamic fracture model represents the initiation and growth of injection-induced hydraulic fractures.

CMG-GEM$^{38}$ is another multiphase, multicomponent single of dual porosity coal bed reservoir simulator. Phase behavior can be described by either the Peng-Robinson or Soave-Redlich-Kwong equation of state. Shape factors can be used to account for flow
between porosities, and additional transfer enhancements can be used to account for fluid placement in the fractures. Mixed gas adsorption is modeled via an extended Langmuir isotherm, and the corresponding diffusion model can be selected based on either concentrations calculated from adsorption characteristics or based on free gas properties. Stress dependent relative permeability changes and matrix swelling and shrinkage can be included.

METSIM$^{2,3}$ is a 3D multicomponent, triple porosity coal bed reservoir simulator. This formulation assumes that there is no water present in macropore system, only free gas exists, and its transport is diffusion controlled. This formulation allows for the competitive desorption in coal by specifying different diffusion time constants for the macropore and the micropore systems. Gas properties are calculated using an equation of state. Multicomponent adsorption is described using an extended Langmuir model. METSIM2 is also coupled to a wellbore and rock mechanics simulator, allowing pore pressure dependent permeability functionality.

**Black Oil Framework**

COMET3 is an extension of COMET and COMET2, developed to model low-rank coal and water saturated gas-shale reservoirs$^{41}$. It can model single, dual, and triple porosity approximation of the coal bed system. In the triple porosity system, gas desorbs from the internal matrix, and migrates to the microporosity matrix and finally to the cleat system where it flows to the wellbore. In this formulation, the microporosity matrix system also models multiphase effects. This accounts for the establishment of a critical gas saturation in the matrix, which may be responsible for a delay in early time gas production observed in some fields. Desorption and diffusion is explicitly modeled. COMET3 can model multiple gas components and accounts for different diffusion rates of the components. An extended Langmuir isotherm is used to model mixed gas adsorption. Pore volume compressibility accounts for stress-dependent porosity and permeability changes. A differential swelling model based on laboratory experiments accounts for swelling attributed to non-CH$_4$ components of the gas.

ECLIPSE-100$^{42}$ is a black oil simulator with additional features for modeling CBM. A dual porosity system is used to model the coal bed system. This simulator is only able to handle two gas components, and therefore it is not able to model an ECBM process with flue gas injection. Compositional effects between CO$_2$ and CH$_4$ are handled by introducing a "solvent" phase. Adsorption is described by the Langmuir isotherm. Eclipse-100 can account for coal shrinkage and compaction effects.

The simulators currently available for aquifer and coalbed storage of CO$_2$ are very capable, with many physical mechanisms represented. They will continue to be very useful for exploring the interplay of physical mechanisms for computational grids of limited size, but they are subject to significant limitations for application at field scale. Conventional finite-difference compositional simulations, even with relatively small numbers of components, are too slow to handle high-resolution representation of the spatial distribution of permeability at field scale, and when coarse computational grids are used instead, they are badly affected by numerical diffusion, which can alter
calculated composition paths in a way that affects calculated performance significantly. Hence, they are probably not suitable for routine simulation of field-scale flows at grid resolutions sufficient to capture the effects of preferential flow paths created by reservoir heterogeneity, especially if the impact of variability in the permeability distribution is to be assessed. For screening of sites, assessment of areas invaded by CO2, or rapid exploration of the impact of injection well placement, simulation tools that are significantly more efficient, but necessarily more limited in the mechanisms represented, are appropriate. One approach, the use of streamline methods, is demonstrated next for two of the geologic settings, gas reservoirs, and aquifers. In the section that follows, we also consider the time scales for dissolution of CO2 in brine in an aquifer and for the equilibration of gas adsorption in a coal bed, summarize work to examine the cooptimization of CO2 storage and performance of an oil recovery process, and we report results of coal adsorption experiments.

**Results**

Compositional streamline methods are based on the idea that the flow can be represented as a series of one-dimensional solutions for multiphase, multicomponent flow along each streamline, with the locations of the streamlines capturing the effects of permeability heterogeneity. In reservoir flows that are dominated by heterogeneity, streamlines move little, and hence streamline locations need be updated only occasionally. In those settings, the streamline approach can be orders of magnitude faster than conventional finite difference computations because the largest computational cost is associated with solving the pressure equation for the streamlines. Effects of gravity segregation and capillary crossflow are not represented in the basic streamline approach, a significant limitation for some reservoir settings. Several investigators have shown that it is possible to represent effects of gravity and capillary pressure in streamline computations by operator-splitting techniques. This approach is reasonable as long as very frequent streamline updates are not needed. Frequent streamline updates are subject to errors that arise from mapping and remapping streamlines, and they eliminate the speed advantage of the approach.

*Combined CO2 Storage and Condensate Vaporization*

CO2 injection into a gas reservoir is a process that can be modeled well by a streamline calculation. The viscosity contrast between injected gas and the gas and condensate in place in the reservoir is small (and the mobility ratio is favorable), and density differences are also relatively small, so streamlines change location slowly compared to the rate at which composition fronts move. The local equilibrium assumption (that fluid phases present at a given location are in chemical equilibrium) is also reasonable for this setting.

To test the use of streamline simulation for CO2 injection in a gas reservoir in which condensate dropout had occurred, we compared streamline simulations with results of ECLIPSE-300 simulations for the same system. In this example, we did not include effects of gravity segregation or capillary crossflow. Analysis of the scaling of these crossflow phenomena suggested that capillary effects were small enough to be neglected,
while gravity effects somewhat larger but still small enough that testing the use of the streamline in the absence of a representation of gravity segregation was reasonable\textsuperscript{43}.

Displacement of a 13-component system was considered. Fluid properties and equation-of-state characterization for the fluid system are reported by Jessen and Orr\textsuperscript{1}. The analytical solution for one-dimensional displacement of this fluid system by pure CO\textsubscript{2} is shown in Figure 13. As the injected CO\textsubscript{2} propagates through the porous medium, it vaporizes condensate, creating a bank of hydrocarbon liquid at the leading edge of the transition zone. The analytical solution is compared in Figure 13 with a series of finite difference simulations for the same problem, with grid resolutions of 100, 500, 1000, and 5000 grid blocks. Comparison of the numerical and analytical solutions indicates that for this compositional problem, the numerical dispersion present in the FD solutions does not resolve the condensate bank unless a very fine grid is used. It is unlikely that use of such fine grids would be attempted in field-scale compositional simulations because the computation times required would be unacceptably large.

![Figure 13: Comparison of analytical solution for 1D displacement of a 13-component gas condensate system by pure CO\textsubscript{2}.](image)

Three finite difference simulations, using identical permeability fields, were performed to assess the magnitude of gravitational effects in this displacement:

- Permeability field oriented vertically, injection at a rate advance of 1.4 \( m/d \) (low rate case).
- Permeability field oriented vertically, injection at a rate advance of 2.8 \( m/d \) (high rate case).
• Permeability field oriented horizontally, injection at a rate of advance of 1.4 m/d.

Predicted recoveries and GORs for these simulations are compared to those for a corresponding streamline simulation in Figure 14. Almost no difference is observed among the simulation results for the different orientations and injection rates, an indication that neglecting the effect of gravity for this flow situation is reasonable.

![Figure 14: Recovery and GOR predictions for 2D displacement simulations.](image)

Between 0.9 PVI and 1.95 PVI, a separation between recovery predicted by the streamline approach and the finite difference simulations is observed. The maximum separation occurs near 1.4 PVI. This difference is due to the production of the condensate bank resolved in the analytical solution but not in the finite difference computations. In this grid, the resolution between injector and producer is 200 grid blocks. In the finite difference simulations of the 1D displacement shown in Figure 13, this resolution was inadequate to capture the effect of the condensate bank. As injection continues, the difference in recovery between the two methods converges to a similar value. Once breakthrough occurs in the streamline method, injection gas cycles through the reservoir, making the displacement increasingly inefficient. Numerical dispersion in the finite difference method smears the front of the displacement, artificially increasing the sweep efficiency in low permeability regions. The velocity of the front is also reduced, delaying breakthrough, as indicated by the difference in GOR between the two methods at later times.
A 3D sector model representing a multi-well gas injection scheme was simulated. The permeability field and well locations for this displacement are shown in Figure 15. Corresponding recovery and total CO₂ storage curves for the sector model are shown in Figure 16. Breakthrough occurs slightly earlier when the displacement is simulated using streamlines. Again, this is related to formation of high flow zones once the displacement front reaches a producer. CO₂ bypasses condensate in the upswept areas resulting in a lower recovery, but high local displacement efficiency in the swept zones. In the FD simulation, dispersion creates a larger reservoir area contacted by the injected CO₂ while the local displacement efficiency in parts of the swept zones is fairly low. The trade-off between sweep efficiency and local displacement efficiency results, for this case, in a higher recovery prediction by the FD simulation, which may very well be artificially optimistic. While the finite difference method and streamline method represent two end members of process recovery (due to low dispersion effects in a condensate displacement), it is likely that the dispersion-free solution used in the streamline calculation more accurately predicts process recovery. The lower sequestration capacity (Figure 16) predicted by the streamline approach is again due to the lower sweep efficiency, a conservative estimate in this example.

![Permeability field and well locations for a 3D sector displacement.](image)

**Figure 15:** Permeability field and well locations for a 3D sector displacement.
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![Graphs showing recovery and sequestration capacity predictions for 3D displacement simulations.](image)

**Figure 16:** Recovery and sequestration capacity predictions for 3D displacement simulations.

Simulation times of compositional finite difference and streamline simulations are summarized in Table II. Speed-up factors observed were on the order of $10^2$-$10^3$. These are dependent on system size. Computational time in a streamline simulation scales approximately linearly with model size, while that of a finite difference method scales approximately as the third power of the number of grid blocks. Therefore, the ratio of times is approximately the square of the number of grid blocks. As the number of active grid blocks simulated increases, speed-up factors increase approximately quadratically.

<table>
<thead>
<tr>
<th>Model Size</th>
<th>FD (s)</th>
<th>SL (s)</th>
<th>Speed Up Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,000</td>
<td>7406</td>
<td>14</td>
<td>499</td>
</tr>
<tr>
<td>13,500</td>
<td>38991</td>
<td>24</td>
<td>1624</td>
</tr>
<tr>
<td>5,774</td>
<td>4446</td>
<td>19</td>
<td>234</td>
</tr>
<tr>
<td>600,000</td>
<td>N/A</td>
<td>1914 (for 1 PV injected)</td>
<td></td>
</tr>
</tbody>
</table>

**Table II:** Comparison of FD and SL simulation times.

For field scale simulation, where the number of gridblocks can be on the order of millions, streamline simulation is the only method currently fast enough to simulate a sequestration project in a reasonable amount of time. Figure 17 shows the results of an optimization study to increase sequestration capacity of a field scale CO$_2$ injection scheme. Sequestration capacity was optimized by changing injection well location and the number of injector wells. The reservoir model contained over 500,000 active grid blocks. Injection of 1 PV was simulated.
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**Figure 17:** Field scale optimization study to maximize production and sequestration capacity. Reservoir model had over 500,000 active grid blocks. Run time of each streamline simulation was less than 10 minutes.

**Cooptimization of CO₂ Storage and Enhanced Oil Recovery**

Previous work demonstrated that the design of combined EOR and sequestration operations differs significantly from the design for EOR alone. For pure EOR, the objective is to maximize oil recovery, while injecting minimum CO₂, and this is typically accomplished by injecting water in some version of a water-alternating gas process. In combined sequestration and EOR, oil recovery and the amount of reservoir volume filled with CO₂ are both to be optimized. Last year’s report summarized our efforts in cooptimization (see also Cakici⁴⁴)

To examine further the cooptimization question, we used a realistic 3D, heterogeneous, and stochastic reservoir description including a 15-component reservoir fluid. These computations were performed using ECLIPSE-300. The reservoir shape is anticlinal, and it is bounded by faults and an aquifer. There are four injectors near the flanks of the reservoir and 4 producers near the crest. The oil is relatively heavy.
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(24°API), and pure CO₂ is not miscible in the crude oil at reservoir pressure. A well control scheme was implemented in the simulator that actively shuts in producers with large gas to liquid producing ratios. This scheme allows gas injection without any water injection. Water injection frustrates cooptimization efforts by filling pore space that could otherwise be utilized for sequestration. Control of wells in this fashion allows the same amount of oil to be produced as in an optimized WAG process (with pure CO₂ as the injectant) while simultaneously storing about 2.5 times as much CO₂ as compared to the WAG.

Despite these promising results, questions existed as to whether the well-control scheme was robust and whether the results obtained with the well control were overly sensitive to the distribution of heterogeneities in the reservoir model. The parameters used to operate the production well are producing gas-oil ratio, injection pressure, and an increase in the allowed producing gas-oil ratio each time a producer is allowed to flow. The initial producing gas-oil ratio and the increment to the gas-oil ratio were chosen in an ad hoc fashion. The sensitivity of performance to values of the allowed gas-oil ratio and its increment were examined through further simulation.

Figure 18 presents the results for the sensitivity analysis of pure CO₂ injection by plotting the variation in the net cumulative recovery, Figure 18a, and reservoir utilization functions, Figure 18b. The y-axis is the producing gas-oil ratio where the production well is first shut in, whereas the x-axis is the increment made to the producing gas oil ratio each time an injection well reaches maximum pressure (350 bar), and producers must be opened to prevent overpressurization of the reservoir. Gray shading represents relatively low values of recovery or utilization, and white represents relatively greater values.

On the one hand, Figure 18 teaches that optimal well control is obtained when the gas-oil ratio where the well is first shut in is set to just slightly above the solution gas-oil ratio (that is the solubility of gas in the oil). This allows control of gas flow at just about the time that gas breaks through to the injection well. Similarly, the results show that increment to the producing gas-oil ratio should be made as small as practical to obtain the best performance.

On the other hand, these results also show that performance of the well-control scheme does not depend critically on control parameters. Note the variations in maximum and minimum values. Differences in recovery and utilization among "best" and "worst" parameters settings differ by 6% to 14%. Thus, the sensitivity analysis indicates that producing gas-oil ratio and injection pressure are robust control parameters. This well-control strategy does not appear to require a high degree of parameter tuning to obtain beneficial results.

Similarly, the sensitivity of results obtained with the well-control scheme was examined as a function of the distribution of permeability within the 3D reservoir model. The injection scenarios include: pure CO₂ injection, WAG with 0.01 PV slugs of CO₂
Figure 18: Sensitivity of (a) net cumulative recovery and (b) reservoir utilization results to well-control parameters. Pure CO$_2$ is injected into 3D reservoir model.
and water, CO\textsubscript{2} injection with well control, and solvent gas (2/3 CO\textsubscript{2} and 1/3 C\textsubscript{2}) injection with well control. Results showed that the oil recovery increased or decreased from model to model, but the best performing production scenario for any given reservoir model is well-controlled injection of solvent. With respect to reservoir utilization, well control with pure CO\textsubscript{2} injection sequesters the most CO\textsubscript{2}. WAG does lead to different sorting of the performances among the reservoir models; however, these deviations from the reference case do not change the conclusion that the well-controlled cases are preferred for cooptimization.

**Time Scales for CO\textsubscript{2} Dissolution in Brine**

At the pressures and temperatures encountered in saline aquifers, the injected CO\textsubscript{2} will form a buoyant gas phase, which will therefore migrate back towards the surface unless migration is inhibited by a geological barrier to vertical flow. To understand whether and if so how much CO\textsubscript{2} might be available to flow vertically, we need to understand how long the injected CO\textsubscript{2} will be mobile. Therefore, we need to understand trapping mechanisms that prevent upward migration by CO\textsubscript{2} and the time-scales over which they operate. If the CO\textsubscript{2} gas phase moves due to its buoyancy or is displaced by invading brine, gaseous CO\textsubscript{2} may be trapped as an isolated residual CO\textsubscript{2} phase. This mechanism will be referred to below as residual trapping. CO\textsubscript{2} has a modest solubility in the aqueous phase, the aqueous CO\textsubscript{2} increases the density of the brine slightly\(^4\), and therefore brine containing dissolved CO\textsubscript{2} will sink rather than rise. We will refer to this trapping mechanism as solution trapping. Figure 19 shows sketches of possible configurations of CO\textsubscript{2} in an aquifer.

![Figure 19](image)

**Figure 19:** Schematic of CO\textsubscript{2} dissolution in two aquifers. The mobile CO\textsubscript{2} gas phase is dark blue, the dissolved aqueous CO\textsubscript{2} is light blue, residual CO\textsubscript{2} is orange, and the brine is not colored. a) CO\textsubscript{2} gas is held under a structural trap. Dissolution of CO\textsubscript{2} into the brine reduces the CO\textsubscript{2} phase volume. b) The CO\textsubscript{2} gas phase migrates along the top of a sloping aquifer, and leaves behind a region of residual CO\textsubscript{2}. In this case both dissolution and residual CO\textsubscript{2} saturation contribute to the decrease of the mobile CO\textsubscript{2} phase.

Reactions of dissolved CO\textsubscript{2} with cations in the brine may ultimately lead to the precipitation of minerals, depending on brine chemistry and aquifer mineral content.
These geochemical reactions have rate constants low enough\(^{145}\) that mineralization reactions will not contribute volumetrically to the trapping of CO\(_2\) in the first several hundred years. However, small changes in porosity due to precipitation may significantly decrease the permeability and help to trap the CO\(_2\) plume dynamically. Residual and dissolution trapping are therefore the likely mechanisms that decrease the amount of mobile CO\(_2\) within the first several 100 years. Residual trapping will only be important if the CO\(_2\) plume moves through the aquifer, and water invades zones containing gas, a likely event as CO\(_2\) from the gas phase transfers to the brine. Dissolution trapping will contribute when CO\(_2\) gas phase is in contact with the brine.

**Convection Enhanced Dissolution**

At the interface between gaseous CO\(_2\) and the brine, CO\(_2\) dissolves into the brine. This dissolution is fast enough that it can be considered to be at equilibrium. The rate of CO\(_2\) dissolution is therefore determined by the transport of CO\(_2\) away from the interface. In the absence of advection, the aqueous CO\(_2\) has to diffuse away from the interface. Ennis-King and Paterson\(^4\) have estimated that the minimum time until a given CO\(_2\) layer is dissolved by diffusion alone as

\[
\tau_{\text{Diff}} \sim \frac{\alpha L^2}{D},
\]

where \(\alpha \sim 10\) is the ratio of the density in the gas phase CO\(_2\) to the mass of CO\(_2\) per unit volume of brine containing dissolved CO\(_2\), \(D \sim 10^{-9} \text{ m}^2/\text{s}\) is the molecular diffusion coefficient, \(L\) is the thickness of the initial layer of gaseous CO\(_2\). For \(L \sim 10 \text{ m}\) the minimum time for dissolution of all CO\(_2\) is of the order of 1 million years. Advection transport of CO\(_2\) away from the interface could increase the rate of CO\(_2\) dissolution and decrease the dissolution time scale by orders of magnitude.

Ennis-King and Paterson\(^4\) report an increase of brine density with increasing aqueous CO\(_2\) concentration. This allows convective transport of CO\(_2\) away from the interface due to buoyancy-driven convection. They argue that the minimum time for dissolution in this case is given by the time it takes for the heavy fingers to propagate a distance \(\alpha L\). Assuming a gravitational velocity \(u_g \sim g \Delta \rho k/\mu\) where \(g\) is the gravitational acceleration, \(\Delta \rho\) is the density difference, \(k\) is the permeability and \(\mu\) is the viscosity of the brine, the time for convective mixing is at least

\[
\tau_{\text{mix}} \sim \frac{\alpha L \mu}{g k \Delta \rho}.
\]

For common aquifers, this time scale is on the order of \(10^4 - 10^5\) yrs, up to two orders of magnitude shorter than the diffusive time scale. Gravity-driven convection may therefore enhance CO\(_2\) dissolution significantly, if it occurs. Convection will only be an effective transport mechanism if fingers of dense CO\(_2\) can migrate significant distances before diffusion eliminates the concentration and hence the density difference. For a
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disturbance with distance \( d \) between adjacent fingers, the diffusive time scale for cross-finger transport is

\[
\tau_{\text{cross}} \sim \frac{(d/2)^2}{D},
\]

so that the length scale of vertical finger propagation is at least

\[
L_f \geq u_g \tau_{\text{cross}} = \frac{gkd^2 \Delta \rho}{4 \mu D} = \frac{10 \cdot 10^{-13} \cdot 5}{4 \cdot 6 \cdot 10^{-4} \cdot 10^{-9}} d^2 \approx 2d^2.
\]

Depending on the wavelength of the disturbance \( d \), \( L_f \) may be smaller or bigger than the required distance for dissolving all CO₂ given by \( \alpha L \).

A mathematical analysis of the instability of the diffusive boundary layer can determine the circumstance under which the diffusive boundary layer will become unstable, subject to the assumptions and boundary conditions used, of course, and give some insight in the initial length scale of the disturbances. Ennis-King and Paterson have presented such a stability analysis of the diffusive boundary layer at the interface between the gaseous CO₂ and the brine. They also performed numerical simulations with the TOUGH2 code that show propagation of CO₂ fingers over tens of meters in 10³ to 10⁴ years. However, the simulations were affected significantly by numerical dispersion, and the numerical grid had a similar or larger length scale than the instabilities in their simulation results. We have reproduced and checked their stability analysis and translated it back into physical space.

To analyze the stability of the boundary layer mathematically, Ennis-King and Paterson have assumed an infinite, homogenous, horizontal layer of depth \( H \). The gaseous CO₂ layer supplying the aqueous CO₂ is neglected. This is a reasonable assumption, because the gravitational instability is between two miscible phases, brine and heavier brine with dissolved aqueous CO₂. They further assume that the density change is small enough so that it can be neglected in all terms except the gravitational term, this is also called the Boussinesq approximation. The governing equations are therefore:

\[
\nabla \cdot \vec{u} = 0,
\]

\[
\vec{u} = -\frac{K}{\mu} (\nabla P - g \rho \hat{z}),
\]

\[
\frac{\partial C}{\partial t} + \vec{u} \cdot \nabla C = \phi D \nabla^2 C,
\]

where \( \vec{u} = (u,v,w) \) is the Darcy velocity, \( P \) is the pressure, \( K \) is a diagonal permeability tensor that may be anisotropic \( (k_x = k_y \neq k_z) \), \( \mu \) is the viscosity of the fluid, \( \rho(C) \) is the density of the fluid, \( g \) is the gravitational acceleration, \( C \) is the concentration of aqueous...
CO₂, φ is the porosity of the porous medium, and D is the coefficient of molecular diffusion of aqueous CO₂ in water. The initial state that is considered is supposed to represent the aquifer some time after CO₂ injection has stopped, and the system has come to rest. The initial condition is therefore \( \tilde{u}(t = 0, \bar{x}) = 0 \), and initially there is no dissolved CO₂ in the brine, hence \( C(t = 0, \bar{x}) = 0 \). The boundary conditions are no penetration for the vertical component of the velocity \( w(z = 0, t) = w(z = H, t) = 0 \) and the concentration has mixed inhomogeneous boundary conditions \( C(z = 0; t) = \frac{\partial C}{\partial z} \bigg|_{z=H} = 0 \). Choosing the following characteristic scales \( C_c = C_0, t_c = H^2/D, x_c = y_c = H^{1/2}, z_c = H, u_c = v_c = \phi D/(H y^{1/2}), w_c = \phi D/H \) and pressure is scaled by \( P_c = \mu \phi D/kv \), where \( \gamma = k_z/k_x \) is the permeability anisotropy, the dimensionless governing equations are

\[
\nabla \cdot \tilde{u} = 0, \quad (8)
\]

\[
\tilde{u} = -\nabla P + \gamma Ra C, \quad (9)
\]

\[
\frac{\partial C}{\partial t} + \tilde{u} \cdot \nabla C = \gamma \nabla^2_H C + \frac{\partial^2 C}{\partial z^2}, \quad (10)
\]

where \( \nabla^2_H = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \), and \( Ra = \frac{\mu \phi D k_H}{\rho \phi D} \) is the Rayleigh-Darcy number. The governing equations only depend on two parameters, the permeability anisotropy \( \gamma \) and the Rayleigh-Darcy number \( Ra \). The initial and boundary conditions for the advection diffusion equation admit the following transient base state solution,

\[
C_b(t, z) = 1 - \frac{4}{\pi} \sum_{n=1}^{\infty} \left( \frac{1}{2n-1} \sin((n - \frac{\gamma}{2}) \pi z) \right) e^{-((n-1/2)^2 \pi^2 t)}. \quad (11)
\]

To study the stability of this base state solution, we introduce small perturbations in concentration and velocity. First we linearize the perturbed equations and subtract the base state. Then we make the plane wave approximation for the shape of the disturbances and obtain two coupled partial differential equations for the amplitude of the velocity and concentration perturbations \( \hat{w} = \hat{w}(z, t) \) and \( \theta = \theta(z, t) \):

\[
\frac{\partial^2 \hat{w}}{\partial z^2} - s^2 \hat{w} + \gamma s^2 Ra \theta = 0, \quad (12)
\]

\[
\frac{\partial^2 \theta}{\partial z^2} - \gamma s^2 \theta - \frac{\partial \theta}{\partial t} - \hat{w} \frac{dC_b}{dz} = 0. \quad (13)
\]

Here \( s \) is the wave number of the two-dimensional perturbations. The system of PDE's is solved numerically, by reducing them to a system of ordinary differential equations (ODE's) using the Galerkin method and then solving the system of ODE's numerically.
The system of coupled ODE’s for the Galerkin coefficients $a_i$ of the concentration disturbance is

$$\frac{da_m}{dt} = A^{-1}(B - \gamma Ra CE^{-1}D)a_i,$$

(14)

where $G_{mli} = G_{ml}(t)$ is a full $N \times N$ matrix, and its coefficients are functions of time. Finally, the average concentration and velocity disturbance can be calculated from the Galerkin coefficients.

The resulting solutions confirm the well-known result that all perturbations decay below a critical Rayleigh-Darcy number. In the context of aquifer sequestration it is useful to fix all physical properties of the aquifer and to think of the $Ra$ number as proportional to the depth $H$ of the layer. For convection to occur, the aquifer needs to exceed a certain critical depth. This depth increases with anisotropy, but is generally less than 15 m for $\gamma \geq 0.01$, $\Delta \rho = 5 \text{ kg/m}^3$, $g = 10 \text{ m/s}^2$, $\mu = 6 \times 10^{-4} \text{ Pa s}$, $D = 10^{-9} \text{ m}^2/\text{s}$, $\phi = 0.2$, and $k = 10^{-13} \text{ m}^2$. All results discussed below will be in terms of this choice of parameters.

An interesting result of this analysis is that above the critical Rayleigh-Darcy number all perturbations decay initially before they start growing exponentially as shown in Figure 20. There is an initial period of stability before the onset of the convective movement. The longer this critical time is, the longer it will take until mixing enhances the CO$_2$ dissolution rate. Ennis-King and Paterson observed, and we confirm, that the critical time is a strong function of the permeability anisotropy, as shown in Figure 21. The critical time increases from tens of years to hundreds of years as the anisotropy changes from $\gamma = 1$ to $\gamma = 10^{-2}$. Even in the worst case this is only a small fraction of the minimum time estimated above to dissolve all CO$_2$ by convective mixing, and therefore only delays it. Finally the stability analysis gives us information about the wavelength $\lambda$ of the perturbations that grow initially. As for depth greater than the critical depth, the wavelength asymptotically approaches a constant value for a given permeability anisotropy. This wavelength increases with increasing anisotropy; our results show a stronger increase compared with those of Ennis-King and Paterson. The initial wavelength is only an indication of the wavelength established in the fully nonlinear system. A rough estimate for the depth of finger penetration is obtained by setting $d = \lambda/2$ in the scaling law for $L_f$. Using our results $\lambda(\gamma = 0.1) \approx 20 \text{ m}$ so $d \approx 10 \text{ m}$, and hence the penetration depth of the fingers is roughly on the order of $L_f \approx 200 \text{ m} \approx \alpha L$. This scaling argument suggests that the instability is strong enough to propagate fingers far enough to mix the dissolved CO$_2$ with a large enough amount of water to dissolve all CO$_2$. 
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Figure 20: The vertical axis shows the average magnitude of the concentration perturbation vs. dimensionless time. The evolution for the disturbance corresponding to a particular wavelength and at a Ra number above the critical Ra number is shown. The disturbance first decays, reaches a minimum, and then grows exponentially. The time required to reach the minimum is the critical time for the onset of the instability.

Figure 21: The vertical axis is critical time for a given permeability anisotropy normalized by the critical time for an isotropic aquifer. This ratio increases as the anisotropy increases. The red line shows the power law fit to the numerical results from Ennis-King and Paterson⁴, the blue stars are our numerical results, and the blue line is the power law fit to our results.
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The analysis discussed here is based on a flow geometry and a set of simplifying assumptions that may not reflect actual aquifer settings. In a typical aquifer the injected CO₂ will flow preferentially through high permeability paths. The interfacial tension between CO₂ and brine will be high, and the viscosity of CO₂ will be significantly lower than that of brine, so CO₂ will displace water inefficiently and vice versa. All of these physical mechanisms will act to increase the volume of brine contacted and the area of contact, which should increase the rate of dissolution. In addition, most aquifers will not be strictly horizontal, and hence there will be some gravity-driven flow in the up-dip direction. This flow will also increase the area of contact. On the other hand, permeability heterogeneity can restrict vertical flow, which would increase dissolution time. Investigation of the interplay of heterogeneity, dissolution, gravity segregation of injected CO₂, slow density-driven convection in the brine phase, and diffusion will require high-resolution numerical solutions for the appropriate combination of mechanisms, a task that is next on our agenda. While the streamline approach demonstrated above can handle effectively the injection period, it is not the appropriate choice for examining the interplay of diffusion, convection, and possible chemical reactions that occur in the long term.

Streamline Simulation of CO₂ Injection in Saline Aquifers

In the previous section, the convection-enhanced dissolution mechanism for trapping CO₂ in an aquifer was discussed. This section focuses on the effect of residual gas trapping on the ability of a given CO₂ plume to migrate upwards and potentially leak to formations above the injection zone.

As CO₂ is injected into an aquifer, the interplay of various parameters including density and viscosity of brine and CO₂ at the prevailing temperature and pressure in the formation will determine the potential for the injected CO₂ to migrate upwards in the formation due to buoyancy. Also, the permeability variations within the aquifer and the presence of any potential flow barriers (shales) will play an important role in the trajectory of the injected CO₂.

Potential sites for CO₂ sequestration in saline aquifers span a wide range of parameter values and accordingly, some of these must be more optimal for long term storage than others. The variation of the viscosity of pure water (similar in behavior to the brine of a saline aquifer) over a fairly narrow range of temperatures can be significant, as Figure 22 shows.

Within the temperature and pressure intervals of probable injection sites, the viscosity of water can vary from 1.25 cp at low temperatures to 0.25 cp at high temperatures. From Figure 22, the modest variation in viscosity with pressure suggests that pressure effects on water viscosity can be neglected in modeling studies as a reasonable approximation. At higher temperatures, the brine in the formation will be more mobile than at lower temperatures, and hence for a given set of rock properties, CO₂ will face less resistance to flow as it displaces brine, suggesting that gravity effects can be more important at these conditions provided that the density difference between brine and CO₂ is sufficiently high. Figure 23 illustrates the variation in CO₂ density with pressure at 313 K and 363 K.
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(for additional isotherms, see McHardy and Sawan⁴⁷. If CO₂ is injected at supercritical conditions, the density can vary from ~200 kg/m³ at low pressures to ~800 kg/m³ at high pressures. The density of water/brine is a relatively weak function of temperature (~1000 kg/m³ at low temperatures to ~960 kg/m³ at the normal boiling point), and it is a weaker function of pressure. Hence a significant upward driving force due to density differences can exist in warm aquifers, where the mobility of water is high relative to cold aquifers, in which the upward migration of CO₂ can be limited by the lower mobility of the brine.

**Figure 22:** Dependence of water viscosity on pressure and temperature⁴⁶.

**Figure 23:** Dependence of CO₂ density on pressure and temperature.
To estimate the magnitude of gravity-to-viscous forces in a given sequestration setting, we adopt the formulation suggested by Zhou et al.\textsuperscript{48}, who define the ratio of gravity to viscous forces by the dimensionless group, $N_{gv}$:

$$N_{gv} = \frac{g \Delta \rho L K_{av}}{H v \mu_w}.$$  \hspace{1cm} (15)

In Eq. (1), $\Delta \rho$ is the density difference between the injected and the resident fluid, $L$ is the displacement length, $K_{av}$ is the average absolute permeability in the formation, $H$ is the height of the formation, $v$ is the injection velocity and $\mu_w$ is the viscosity of the initial fluid in the formation (water). To map out the potential range of sequestration scenarios, Table III reports estimates of low and high values of the individual components of Eq. (1) and the corresponding value of the gravity to viscous number $N_{gv}$.

<table>
<thead>
<tr>
<th>Estimate</th>
<th>$\Delta \rho$ (kg/m$^3$)</th>
<th>L (m)</th>
<th>H (m)</th>
<th>$K_{av}$ (mD)</th>
<th>v (m/day)</th>
<th>$\mu_w$ (cp)</th>
<th>$N_{gv}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td>800</td>
<td>1E5</td>
<td>200</td>
<td>1000</td>
<td>10</td>
<td>1</td>
<td>33.5</td>
</tr>
<tr>
<td>Low</td>
<td>200</td>
<td>1E3</td>
<td>10</td>
<td>1</td>
<td>0.1</td>
<td>0.2</td>
<td>0.84</td>
</tr>
</tbody>
</table>

From the reported estimates of high and low values of the gravity to viscous forces, we find that depending on the temperature and pressure of the aquifer (as well as the permeability and injection rates), we might expect to see a full range of flow patterns within the various aquifers from gravity-dominated flow to viscous-dominated flow. In the following subsection, we investigate the effect of changes in fluid properties with temperature and the significance of residual trapping.

To test our qualitative scaling argument, a series of example calculations was performed. All were done with the Stanford compositional streamline simulator, CSLS. The simulator describes the phase behavior of the CO$_2$–brine system by a modified version of the Peng-Robinson equation of state\textsuperscript{2}. Special care must be taken to account properly for the mutual solubility of CO$_2$ and brine. Our approach follows the modifications outlined by Yan et al.\textsuperscript{49}. Temperature-dependent shift parameters are used to ensure accurate prediction of phase densities. Simulation of CO$_2$ injection in the formation shown in Figure 24 was performed at two temperatures to evaluate the impact of variations in fluid properties.
The formation is a 6000 m by 189 m cross-sectional area of an aquifer consisting of 5 high-permeability (3000 mD) sand compartments separated by low-permeability shales (3 mD). The porosity of the sands is 35% whereas the porosity in the shales is 3.5%. The simulation grid is 100*62, a bit on the coarse side, but sufficient to investigate variation in flow patterns with temperature. Corey type relative permeability curves were used with an irreducible brine saturation of 0.2. The same relative permeability curves were used for the sandstones and shales. The first example simulation was performed at 313 K (40°C). The sequestration process was simulated for two years for four values of the critical gas saturation (0, 0.05, 0.1 and 0.2). Figure 25 reports the fluid distribution at the end of the injection phase.

As the residual gas saturation is gradually increased, the tendency for the CO2 to follow the preferential flow paths below the shales decreases. Also, the significance of the gravity override decreases as gas is trapped with increasing \( S_{gc} \). From Figure 25, it is clear that the critical gas saturation can play an important role in preventing the free CO2 from migrating to the top of the formation. Comparison of the locations of the gas fronts in the top \( (S_{gc} = 0) \) and bottom panels \( (S_{gc} = 0.2) \) of Figure 24 indicates that the increase in \( S_{gc} \) must result in an increase in the amount of CO2 that is dissolved in the brine. Figure 26 reports the concentration maps for two of the displacements illustrated in Figure 25. It confirms the observation that although a smaller volume of the brine is contacted by CO2 at high \( S_{gc} \), the concentration of CO2 in the contacted brine is higher than for \( S_{gc} = 0 \). For comparison with the second set of displacement calculations, we note that the ratio of gravity to viscous forces for the low temperature displacements is estimated to \( N_{gv} = 4.1 \).

In the second set of displacement calculations, the temperature of the aquifer was set to 363K (90°C). Accordingly, the viscosity of the brine is reduced from \( \sim 0.653 \) cp to \( \sim 0.276 \) cp, while the viscosity of CO2 declined from 0.05 to 0.025 cp. In this displacement the gravity-to-viscous ratio was \( N_{gv} = 21.1 \). Figure 27 demonstrates that there is a more significant impact of gravity segregation at the higher temperature. As for the low temperature calculations, the sequestration process was repeated for four levels of
Figure 25: Gas saturation after two years of injection (T = 313K).
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**Figure 26:** Mole fraction of CO₂ dissolved in the brine (T = 313K)

critical gas saturations, $S_{gc}$ (0, 0.05, 0.1 and 0.2). The results of the simulations after two years of injection are reported in Figure 27. For the high temperature (high mobility of brine) we find a significant increase in the predicted gravity override. Four factors contribute to the increase in gravity segregation: (a) the gas phase is less restricted to flow in the vertical as well as the horizontal direction due to the decrease in brine viscosity, (b) the density difference between the injected CO₂ and the brine has increased as the CO₂ now has a density of ~260 kg/m³ as opposed to the low temperature displacement where the injected CO₂ had high density of ~670 kg/m³, (c) at the higher temperature, the solubility of CO₂ in the brine is lower resulting in a larger volume of mobile low-density gas in the formation, and (d) the ratio of water viscosity to CO₂ viscosity increases at the higher temperature, resulting in a lower local displacement efficiency.

The simple scaling arguments and examples presented here, demonstrate the impact of the fluid properties in an aquifer injection process on the tendency of the injected CO₂ to migrate upwards in the formation. The examples also confirm the utility of the streamline simulation approach for this problem. Numerical solutions were used along streamlines, which were updated periodically, as gravity segregation shifted streamlines. Each simulation took about ten minutes of computation time. Those simulations can be performed at low enough cost in computation time that the interplay of heterogeneity,
trapping, and solubility can be explored in detail for the injection period of an aquifer storage project.

\[ S_{gc} = 0.0 \]

\[ S_{gc} = 0.05 \]

\[ S_{gc} = 0.10 \]

\[ S_{gc} = 0.20 \]

\[ S_{gas} \]

\[ 0 \quad 0.1 \quad 0.2 \quad 0.3 \quad 0.4 \quad 0.5 \quad 0.6 \quad 0.7 \quad 0.8 \]

**Figure 27**: Gas saturation after two years of injection (T = 363K).
Time Scales for Coalbed Sequestration

Enhanced coal bed methane (ECBM) recovery combined with CO₂ storage is one option for sequestration of CO₂. Flow through coalbed reservoirs occurs in a network of subparallel face cleats orthogonally intersected by butt cleats. For a mature, high-rank coal, typical cleat aperture is approximately 0.1 mm, and typical cleat spacing is 1-2 cm

When CO₂ is injected, it flows through the cleat system and diffuses into the matrix. Preferential adsorption of CO₂ causes adsorbed CH₄ to desorb. The desorbed CH₄ then diffuses through the matrix to the cleat system, where it flows to the production well and is produced. Diffusion through the matrix is controlled by concentration gradients, while flow through the cleat system is controlled by pressure gradients. The rate of production from coalbed reservoirs is controlled by the slower of these two processes. In this section, we consider the question of whether it is appropriate to model field-scale flow in a coalbed with an assumption of local chemical equilibrium between coal and gas or whether some more complex model is required.

The following simple scaling analysis examines the effect of diffusion transport in the cleat and matrix systems. In cases where convection dominates, the local equilibrium assumption is reasonable. If the local equilibrium assumption can be made, then the cleat network controls flow through coal bed reservoirs, and the details of matrix diffusion effects need not be represented explicitly.

Cleat System. Flow in the cleat system can be described by the convection-dispersion equation shown in Eq. 16, which describes the concentration of injected gas in the fracture system, \( C_f \). The Peclet number (\( Pe \)), defined in Eq. 17, is a ratio of the characteristic time for diffusion to the characteristic time for convection.

\[
\frac{\partial C_f}{\partial \tau} + \nabla \cdot C_f - \frac{1}{Pe} \nabla^2 C_f = 0, \tag{16}
\]

where

\[
Pe = \frac{vL_f}{D_f}, \tag{17}
\]

and \( \tau \) is dimensionless time, \( v \) is the average flow velocity in the fractures, \( L_f \) is the displacement length, and \( D_f \) is the diffusion coefficient in the gas phase in the fractures. Large values of \( Pe \) characterize convection-dominated flows. For typical ECBM displacements, \( Pe \) is very large. For a flow velocity of 0.33 m/d, a flow length of 400 m, and a diffusion coefficient in the gas of \( 10^{-4} \) cm²/s, for example, the resulting Peclet number is \( 1.5 \times 10^5 \). That value is large enough that it is quite reasonable to neglect the effects of longitudinal diffusion in the flow calculation.

Matrix System. In the coal matrix system, we assume that diffusion is the only mechanism of transport. The conservation equation is

\[
\frac{\partial C_m}{\partial t} = \nabla \cdot D_m \nabla C_m, \tag{18}
\]
where \( C_m \) is the concentration of injection gas in the matrix and \( D_m \) is the diffusion coefficient in the matrix. Diffusional transport was considered for a dry matrix and a wet matrix. For the dry matrix, diffusion through a single matrix block was considered. The system was reduced to an equivalent spherical system, and a constant diffusion coefficient was assumed. For a spherical coordinate system, Eq. (3) becomes

\[
\frac{\partial C}{\partial t} = \frac{D_m}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C}{\partial r} \right),
\]

(19)

with boundary conditions

\[
C(r = R, t) = 1,
\]

(20)

\[
C(r, t = 0) = 0.
\]

(21)

The time required for the average concentration in the sphere to reach 95% was calculated. The resulting diffusion time as a function of effective diffusion coefficient and radius of the sphere is shown in Figure 28. The time required for equilibration depends fairly strongly on the assumed diffusion coefficient. Shi and Durucan report values, estimated by fitting effluent composition data for pulverized coals, of \( 5 \times 10^{-8} \) to \( 5 \times 10^{-6} \text{ cm}^2/\text{s} \) for micropores and \( 2 \times 10^{-5} \) to \( 7 \times 10^{-4} \text{ cm}^2/\text{s} \) for macropores. Thus, for large diffusion coefficients, equilibration time for all radii of sphere considered is on the order of days. For small diffusion coefficients, equilibration time is a function of the radius of the system, ranging from a few days for spheres with a 1 cm radius, to months for spheres

\[\text{Figure 28: Time required for the average concentration to reach 95\% in a sphere of dry coal. Typical matrix size for a mature coal is 1-2 cm.}\]
with a 5-cm radius. For a high rank coal, where fracture spacings are small, equilibration time is on the order of tens of days for a typical solid diffusion coefficient of $10^{-7} \text{cm}^2/\text{s}$.

Coal reservoirs are typically water saturated, and the coal surface is water wet. In this system, for mass transfer between matrix and fracture systems, we assume that gas must diffuse through a thin film of water. The presence of water creates extra resistance to mass transfer. The concentration gradient driving mass transfer in the water phase is relatively low, because the solubility of gas in the water limits the concentration gradient in that phase.

Figure 29: Schematic of a simplified wet matrix system.

For this calculation, the wet matrix was approximated as a spherical film of constant thickness, surrounding the matrix (Figure 29). The time to reach the 99% of the solubility concentration at $r_a$ is presented as a function of diffusion coefficient and film thickness in Figure 30. For the range of thicknesses and diffusion coefficients considered, film equilibration times are very short (on the order of minutes) compared to matrix equilibration times. Diffusion coefficients for CO$_2$ in water at high pressure are on the order of $10^{-5} \text{cm}^2/\text{s}$. Hence we conclude that for a typical cleat aperture of 0.1 mm, the time required for diffusion through a water film with similar thickness is small compared to the other characteristic times for flow and equilibration.

This simple analysis of diffusion in the cleat and matrix system suggests that diffusion times are short enough that for flow at field scale, it is a reasonable approximation to assume that the fluid in the cleat system is in equilibrium with the solid. If so, then the problem of representing adsorption of CO$_2$ and other gases in a coalbed revolves around accurate representation of the multicomponent adsorption. If a suitable model of that adsorption is available, it should be possible to take advantage of the speed of streamline simulation techniques for this system.
Enhanced Coalbed Methane Recovery and CO₂ Sequestration

The relatively advanced state of knowledge regarding the mechanisms of EOR is not matched for gas injection into coalbeds. Our previous analytical study of the flow of multicomponent gases through dry coal (Zhu et al.⁸) revealed the strong coupling between the advance of a gas species and its adsorption properties. It was predicted that coals are capable of separating CO₂ from N₂, among other results. Experimental verification of model predictions appears prudent before adding more detail to the calculations.

An experimental program was begun with the goals of validating prior flow and adsorption predictions as well as developing a database for comparison of more advanced predictions. The apparatus developed is illustrated in Figure 31. The centerpiece is the core holder for holding coal samples that are 4.25 cm in diameter and up to 25 cm long. To date, we have employed crushed (60 mesh) and dried coal samples from the Powder River Basin. The crushed coal is packed to obtain a porous medium with a permeability of 80-100 md and a porosity of 0.33. The apparatus is capable of using intact core samples, but no field samples available to us had sufficient integrity to be employed directly.
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Coal surfaces are equilibrated with methane at a given pressure, typically between 500 and 750 psi. The displacement gas is a mixture of CO₂ and N₂, and its flow is metered by a 0-50 SCCM (standard cubic centimeters per minute) mass flow controller. The concentration of gas components (CO₂, CH₄, N₂) in the effluent and at sampling ports along the length of the core is measured with a gas analyzer to ±0.01%. The rate of gas production is also measured as is pressure drop along the core. A backpressure regulator maintains the outlet of the system at constant pressure.

A first step in the investigation was the measurement of the adsorption and desorption properties of pure CO₂, CH₄, and N₂ on the coal. Measurement results are given in Figure 32. Several notes are in order. First, CO₂ was the most strongly adsorbing gas. At 800 psi, roughly 3 times as much CO₂ adsorbed as did CH₄ and more than 8 times as much CO₂ adsorbed as did N₂. Second, there was significant hysteresis among adsorption and desorption results. Upon depressurization, coal retained significant volumes of gas. At 220 psi, this coal retained 80% of the CO₂ that had adsorbed at 800 psi. The hysteresis between adsorption and desorption characteristics does not yet have a satisfactory physical explanation. Nevertheless, the difficulty in desorption of CO₂ suggests that coal may be a secure site for CO₂ sequestration.

Figure 31: Schematic of experimental apparatus.
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A suite of displacement experiments is underway to be used subsequently to interpret ECBM and sequestration mechanisms and thereby to provide a first step in improving conceptual and mathematical models. Some representative results follow. Figure 33 provides a comparison between pure N₂ and CO₂ as injection gases. The figure shows the composition of gas exiting the coal versus the amount of gas injected in pore volumes (PV) computed at the outlet pressure of the coal. Comparison of Figures 33(a) and (b) shows that injected N₂ broke through to the exit in about 0.4 PV whereas CO₂ did not appear until after 1.5 PV of total gas had been injected. Note also that a significant fraction of the CH₄ produced as a result of N₂ injection was mixed with N₂. About 3 PV of total injection was required to sweep out the CH₄ with N₂. Production of CH₄ as a result of CO₂ injection was virtually complete when CO₂ broke through at 1.5 PV, and there was little production of CH₄/CO₂ mixtures. Permeability of the pack decreased by 34% as CO₂ replaced CH₄. Total recovery of the initial CH₄ in the system was 77% with N₂ injection and 92% as a result of CO₂ injection. With respect to recovery, breakthrough time, and the mixing of injection gas and CH₄, CO₂ is the superior injection gas.

Injection gases with various concentrations of CO₂ and N₂ have also been tested. Figure 34 shows the production profiles resulting from an injection gas with 23.5% CO₂ and the balance N₂. Such a mixture might be similar to a combustion gas enriched in CO₂ but not separated completely. Notably, N₂ broke through at the outlet in roughly 0.4 PV, and its concentration increased rapidly thereafter; however, CO₂ did not appear until...
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Figure 33: Production profiles for pure gas injection into a Power River Basin, WY coal sample: (a) pure N₂ injection gas and (b) pure CO₂ injection gas. The system backpressure is 600 psi. Injection rate is 0.5 SCCM.
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Figure 34: Production profile for gas injection into a Powder River Basin, WY coal sample. Injection gas is 23.5% CO₂ and 76.5% N₂. The system backpressure is 600 psi. Injection rate is 0.5 SCCM.

After 3.3 PV of injection and the fraction of CO₂ in the produced gas always remained low. The coalbed effectively separated the N₂ and the CO₂ in the injection gas. The total CH₄ recovery for this experiment was 80%.

Should such laboratory results for injected gas mixtures prove relevant to the field scale, they indicate a clear tradeoff between the compression required to elevate the mixed gas to injection pressure and the cost to separate CO₂ from N₂ on the surface prior to injection. Note that the experiments also suggest that N₂ may have to be separated from produced CH₄ for a significant period of the total production period with either the injection of pure N₂ or a mixture containing significant N₂.
II.3.3 Geophysical Monitoring of Geologic Sequestration

Investigators
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Background
Subsurface monitoring will be required to provide: (1) early warning of reservoir leaks to address public safety concerns; (2) images of the space-time distribution of injected CO\textsubscript{2} to aid optimization of injection and storage; and (3) input to the safety case analysis expected to be required for a permit and licensing process. Geophysics offers a variety of methods that operate over a wide range of geological environments, reservoir scales, and depths. The challenge is to track the flow of CO\textsubscript{2} while simultaneously monitoring for leaks in a growing subsurface volume. Moreover, a thorough description and predictive simulation of the monitoring capability may be required for the safety case when a site is presented for licensing.

During the initial phase of the study, we developed models that estimate the changes in bulk rock-fluid properties with injected CO\textsubscript{2}. We then considered several geophysical monitoring methods, e.g., seismic, electrical, magnetic, electromagnetic, gravity, and surface deformation (Wynn\textsuperscript{54}) and performed sensitivity analyses for each. See summary below. The major conclusion of this initial study was that seismic methods provide the most effective and universally applicable technology for subsurface monitoring for the various geologic storage scenarios of coal beds, deep saline aquifers and depleted oil and gas fields. However, seismic imaging, as we know it from the petroleum industry, is too expensive for continuous or repeated long-term monitoring. Our ongoing research is focusing on the development of cost-effective time-lapse seismic imaging techniques that can potentially provide quasi-continuous monitoring and adapt to address safety concerns. We’re following the guiding principle that the monitoring effort must decrease with time, barring a reservoir problem, and eventually cease altogether when safe containment is no longer a concern.

Summary of Subsurface Monitoring Options
This section summarizes the results of our scoping study on the applicability of various geophysical methods for monitoring CO\textsubscript{2} sequestration. The details of this study are given in Wynn\textsuperscript{54}. He explored the available options for monitoring formations undergoing CO\textsubscript{2} injection. Rock physics models were used to determine the time-lapse changes in relevant physical properties (acoustic, electrical, etc.) for a variety of rock types at the pore scale. These rock physics models were used in a synthetic formation model to estimate field or measurement scale changes. Results from different settings were compared to suggest optimum monitoring techniques for monitoring geologic sequestration. Also examined were the potential uses of each technique for monitoring CO\textsubscript{2} migration, seal integrity, and mass balance. Seismic, electromagnetic, gravitational, and geodetic methods are the four broad types of subsurface geophysical monitoring examined. Direct sampling methods such as monitoring wells have high spatial resolution.
but low spatial coverage. Subsurface geophysical imaging techniques generally have high spatial coverage with limited spatial resolution, but have the added benefit of being remote. While a monitoring well would have to penetrate the formation seal to gather meaningful hydrologic data or fluid samples, possibly creating conduits for CO₂ to escape, seismic imaging may be used to image the area of interest without such intrusion.

In seismic monitoring, the changes we may detect are changes in velocity, reflectivity, and possibly attenuation. The bulk of the velocity changes resulting from saturation effects occur with only a small amount of CO₂ in the pore space. For this reason seismic monitoring will be very useful in leak detection and for monitoring CO₂ migration. Seismic monitoring should be able to detect thin layers of CO₂, under favorable circumstances meaning that migration paths should show up in a reflection survey and the presence of CO₂ in overlying zones should be easily detectable. The acoustic velocity of fluids under most reservoir conditions is typically above 1000 m/sec, whereas the velocity of CO₂ is considerably less. Figure 35 shows velocities of CO₂ at different pressures and temperatures. Figures 36 and 37 are examples of wave velocity changes in CO₂ flooded sandstone and CO₂ flooded coal. The velocity change due to CO₂ flooding is significant, which favors the seismic monitoring.

Resistivity surveys are the simplest method of assessing subsurface conductivity. At the large separation distances required for monitoring CO₂ sequestration such techniques will detect only the average changes in the reservoir and may be of too low resolution to be of any use. Another option is crosswell electromagnetic measurements. At the low frequencies necessary to propagate EM waves across field scale distances the resolution is fairly low, and the measurements are strongly affected by the conductivity structure near the source and receiver.

![Figure 35: P-wave velocities of CO₂ (Wang and Nur⁵⁵).](image)
Figure 36: P-wave velocities in hydrocarbon-saturated and CO2-flooded sandstone. Black lines are isotherms for hydrocarbon-saturated rocks, and blue lines are isotherms for flooded rocks. Confining pressure for the plots is 20 MPa (Wang and Nur55).

Figure 37: Predicted P-wave velocities in a CO2-flooded coal from Gassmann’s equation (Gassmann56) and laboratory data from Yu et al.57.

Gravity monitoring is only suitable for making very low-resolution mass balance measurement, and that too in shallow formations as the signal falls off inversely with distance squared. Geodetic techniques measure displacements or displacement gradients at the earth’s surface. Such techniques are commonly used in the study of earthquakes or volcanoes but may also have limited applications in monitoring CO2 sequestration under
II.3 Project Results: Geologic CO\textsubscript{2} Sequestration

certain conditions. In a stable tectonic environment, measured deformation over a sequestration site should only be the result of induced pressure changes at depth due to fluid injection. However, surface geodetic techniques, much like gravity, are very low-resolution techniques.

The results of Wynn’s\textsuperscript{54} study are summarized in Table IV. Not surprisingly seismic, being a versatile, high-resolution technique has the widest range of uses and is not limited by geologic setting. The SACS project at Sleipner has certainly confirmed the ability of seismic monitoring to track CO\textsubscript{2} in the subsurface.

Table IV: Summary of the usefulness of geophysical techniques by use and setting.

<table>
<thead>
<tr>
<th></th>
<th>Seismic</th>
<th>Electromagnetic</th>
<th>Gravity</th>
<th>Deformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Balance</td>
<td>low res.</td>
<td>low res.</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>CO\textsubscript{2} Migration</td>
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<td>good</td>
<td>low res.</td>
<td>low res.</td>
</tr>
<tr>
<td>Leak Detection</td>
<td>good</td>
<td>good</td>
<td>low res.</td>
<td>no</td>
</tr>
<tr>
<td>Geologic Setting</td>
<td>any</td>
<td>aquifers</td>
<td>any</td>
<td>oil and gas</td>
</tr>
<tr>
<td>Rock Strength</td>
<td>any (soft better)</td>
<td>any</td>
<td>any</td>
<td>soft</td>
</tr>
<tr>
<td>Formation Depth</td>
<td>any</td>
<td>any</td>
<td>shallow</td>
<td>shallow</td>
</tr>
</tbody>
</table>

Adaptive Seismic Monitoring: A New Approach to Time-Lapse Subsurface Imaging

Our proposal for subsurface CO\textsubscript{2} monitoring is to trade the conventional approach of high spatial/low temporal resolution for a new approach providing low spatial/high temporal resolution monitoring. The premise upon which this approach is based is that the high-resolution features are predominately static and do not change significantly during the injection cycle of the storage process. We are developing strategies for seismic imaging though the approach is applicable to other imaging methods as well. The conventional seismic approach (Figure 38) that’s used for hydrocarbon reservoirs is to produce a temporal sequence of high-resolution images or snapshots $m_i$, taken years apart as reservoir development progresses. Changes in the reservoir are detected by differencing the snapshots. For many reasons the differences often have much lower resolution than the individual snapshots, e.g., data acquisition is not repeatable and true reservoir changes are often larger scale. Our new approach (also Figure 4) is designed to build upon the high-resolution baseline image (produced as part of the site-selection process) with a sequence of low-resolution difference images $\Delta m_i$, each taken perhaps months or even weeks apart. To maximum acquisition repeatability, we propose to instrument the storage field with permanently emplaced seismic sources and detectors. To accelerate data processing and data analysis, the time-lapse data sets are recorded with reduced spatial and temporal sampling and coverage. The smaller data are then processed to explicitly parameterize a time-varying reservoir model (Day-Lewis \textit{et al.}\textsuperscript{58}). Changes in fluid saturation (without the high-resolution static background) are directly imaged rather than through difference images. Moreover, we propose new survey geometries, acquisition schemes, and processing methods that are aimed at reducing costs and providing quasi-real-time monitoring capability. We are calling this new approach Adaptive Seismic Monitoring (ASM).
II.3 Project Results: Geologic CO₂ Sequestration

**Figure 38:** The conventional time-lapse imaging approach is to produce a sequence of snapshots, $m_i$, each taken perhaps years apart, e.g., $m_0$ and $m_1$ in the upper figure. Our new approach (ASM) is to produce a larger sequence of lower resolution difference images, $\Delta m_i$, taken perhaps months or even weeks apart. The baseline image $m_0$ is the same in both cases and comes from the site selection and characterization study.

An example of a new acquisition strategy is the Stanford Cross-Linear array illustrated in Figure 39. Seismic sources and detectors are distributed along three linear arrays, two along the surface and one along the injection borehole. The 3-axis arrays provide reduced 3-D resolution, but at greatly reduced acquisition and processing costs relative to the usual 2-D surface array. Both sources and receivers are permanently embedded to maximize survey repeatability and reduce deployment costs. Additional surface lines may be added or different sections of the Cross may be activated at different times to track the CO₂ front or to target specific reservoir zones or problems areas. Our new approach includes signal coding to permit the use of low-power sources for continuous operation; these attributes in particular enable quasi-real-time monitoring.

**Figure 39:** The Stanford Cross-Linear array incorporates 3-axis linear source/detector arrays emplaced along the surface and embedded along the injection borehole. Both in-plan and out-of-plane imaging is possible with this configuration. Sampling and the dimensions of the apertures of the arrays may be adjusted for resolution and subsurface coverage.
Results

A Synthetic Study on Seismic Monitoring

In order to test the many possibilities, we have developed some modeling tools for simulating the imaging of seismic data. So far, we are performing tests in two spatial dimensions. In this section, we present results for simulation study on full aperture imaging. During the next phase of the project, we will move to three spatial dimensions and limited aperture simulations. The synthetic model simulates shallow reservoir sands (e.g., less than 1000m) with a porosity of 35%. Four snapshots of the seismic velocity before and during CO2 injection are shown in Figure 40. During injection, CO2 replaces water in the formation resulting in assumed saturation levels of 20% CO2 and 80% water. The P-wave velocity decreases from the pre-injection value of 2000 m/s to the post-inject value seen in the plumes of 1270 m/s. The changes in velocity are estimated using Gassmann’s equation (Gassmann56). Spatial dimensions, reservoir geometry, and seismic properties of the model are intended to be similar to those found at Sleipner.

We computed seismic datasets for each of the reservoir images shown in Figure 6. Each dataset was then processed using prestack depth migration (e.g., Bleistein & Gray59) as the imaging method. The resulting time-lapse images of seismic reflectivity, shown in Figures 41, clearly show signatures of CO2 saturation. Indeed the synthetic images show a skeletal resemblance to the time-lapse images from Sleipner, albeit with fewer details. We can see from Figure 41 that the amplitude differences in the time-lapse images indicate the changing contrast in reflectivity associated with changing CO2 buildup just below impermeable horizontal interfaces. While there are also some imaging artifacts, the effects of the CO2 are easily distinguished in these full aperture images. One of the imaging artifacts is the downward shift in the apparent depth of reflectors below CO2 saturated zones. While an artifact of the image generation (wrong velocity), this downward shift may be used in a feature extraction scheme for real-time leak detection.

Figure 40: Four snapshots from a synthetic model of a reservoir experiencing CO2 injection: (a) before injection; (b)–(d) three subsequent snapshots after injection illustrate the evolution of low velocity plumes of CO2 generated as CO2 migrates upward through shale breaks and accumulates below low permeability barriers.
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Figure 41: Time-lapse seismic images of the storage reservoir undergoing CO₂ injection. The images were created using prestack depth migration and full aperture datasets. (a) baseline; (b) – (d) time-lapse images (left column) and difference images (right column).
Diffraction Tomography

The simulations described above demonstrate that our modeling tools are fully capable of realistically capturing the effects of CO2 seen in field data. Nevertheless, these realistic tools are much too complicated and slow to explore the parameter space required to develop Adaptive Seismic Monitoring. In order to study the important issues, we need a rapid way of investigating the effects of sampling, aperture dimensions, and signal frequency and bandwidth on image quality. To that end, we are using diffraction tomography based on the Born approximation as a solution to the Helmholtz equation (Devaney\textsuperscript{60}, Harris\textsuperscript{61}, and Wu and Toksoz\textsuperscript{62}). While this method is elegant and especially useful for the simulation problem at hand, it has also been used on 2-D and 3-D field datasets (Bleistein and Gray\textsuperscript{63}, Keho and Beydoun\textsuperscript{64}, Louie \textit{et al.}\textsuperscript{65}). To differentiate the two imaging approaches presented here, diffraction tomography is best described as providing a quantitative velocity inversion based on weak inverse scattering theory while prestack depth migration is a qualitative “transpose” method based on back propagation. Diffraction tomography images the changes in velocity in the volume whereas migration images the changes in reflectivity at interfaces. Both have strengths and weaknesses. We needn’t decide which to apply for the real-world monitoring problem at this time. While migration is far more practical for large field datasets, the analytical elegance of diffraction tomography is more useful for addressing the design problems of adaptive monitoring.

We assume that we have a baseline high-resolution seismic dataset prior to the injection of CO2. The seismic wavefield used to produce the baseline image is denoted $U^o(r)$. When CO2 is injected, the wavefield is perturbed to $U^i(r)$. The difference between the two is the scattered field $U^s(r)$ that’s generated by the injected CO2. It can be shown that the scattered wavefield is linearly proportional to the Fourier spectrum of the changes in the medium created by the CO2:

$$U^s(\hat{r}, \hat{s}) = U^i - U^o \approx \frac{U^o k^2}{4 \pi r} e^{i k r} \int_{\nu} O(r') e^{-i k r'} d r' = \frac{U^o k^2}{4 \pi r} e^{i k r} \tilde{O}(k_s), \quad (22)$$

where $\tilde{O}(k_s)$ is the Fourier transform of the perturbation in the medium $O(r)$ caused by the CO2. The scattering vector $k_s = (\hat{r} - \hat{s}) c/\omega$ is used to define the set of angles and frequencies that can be used to sample the Fourier support of the medium with a combination of source and detector locations and signal frequencies. We use the spectral support as a filter to obtain a bandlimited spectrum of the medium. Inverse Fourier transform of the bandlimited spectrum gives a reconstruction of the medium for the considered geometry of sources and detectors and frequency bandwidth. Figure 42 shows the result of applying filters corresponding to surface seismic source-receiver apertures.
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Figure 42: Time-lapse simulation from diffraction tomography: (a) Original earth model; (b) Diffraction tomogram for (a); (c) Spectral filter for a relatively wide surface seismic aperture; (d) Earth model with CO$_2$; (e) Diffraction tomogram of (d); (f) Difference tomogram. These images illustrate the ability of diffraction tomography to detect volumetric changes unlike migration that detects changes at the interfaces.

**Barriers and Issues to large scale monitoring:**

After years of injection, significant amounts of undissolved CO$_2$ could extend several kilometers laterally, potentially finding leakage pathways far away from the injection wellbore. These potential leak paths include abandoned boreholes and geological features such as faults and fractures in the subsurface. Monitoring must cover a significant portion of the reservoir if not the entire storage volume. Nevertheless, monitoring should not continue indefinitely nor should continuous monitoring be required during the entire life of the injection cycle. The questions of how much monitoring, how long and how often have not been answered and are expected to be responsive to regulatory and safety issues. Although monitoring costs may be relatively small in comparison with capture and transportation costs, they are nonetheless real expenses associated with disposal of a waste material. Efforts to improve the technical capability and reduce the direct cost of monitoring should be rewarded with easier public acceptance and truly safer reservoirs. It will be important to include monitoring as an integrated part of the site-specific sequestration project and begin the monitoring process with the baseline characterization study.

The ability to monitor a reservoir should be one of the many criteria considered when selecting a storage site. Also, the capability to predict the behavior or simulate the monitoring process is expected to be an important site-specific licensing issue. We have some concern regarding the conflicting requirements for leak detection and other safety issues (monitoring the entire storage volume) versus monitoring to assess process efficiency, i.e., following the front to track where the CO$_2$ is going. For this concern
alone, the monitoring strategy must be adaptive to meet changing resolution and coverage requirements with time. This is the guiding principle of our adaptive seismic-monitoring approach.

**Progress**

In the area of assessment of seal integrity, the projects are all beginning to take form. The biggest step we have made this year is developing important collaborations with a number of different companies, laboratories, and individuals. From these, we have gained resources, data and individual expertise and guidance that will aid in the success of our projects. Taken together, our three projects cover all of the possible options for geologic CO$_2$ sequestration. This will provide a meaningful breadth to our work. Individually, the projects will look deeply into the geomechanical issues unique to each specific setting. We are clearly moving towards a better understanding of how geomechanics influences the seal capacity, integrity and sequestration potential in the three geologic CO$_2$ storage options. This is a fundamental step in making widespread CO$_2$ sequestration operations a reality. Only through large-scale implementation will CO$_2$ sequestration make a significant impact in stabilizing atmospheric CO$_2$ concentrations.

In the area of flow prediction, we have completed a review of simulation tools available for CO$_2$ sequestration, and we now have working code available for compositional simulation of sequestration in gas fields, with or without condensate present. We also have a model working for streamline simulation of the injection period of aquifer sequestration with dissolution of CO$_2$ in the brine and gravity segregation. We are engaged presently in work to understand the interplay of physical mechanisms that act on various time scales for aquifers and coalbeds. Those analyses will guide the selection of simulation methods and tools that will be the toolkit for designers of sequestration projects. In some areas, continued development of the streamline approach will be useful, but for others, other simulation tools will be required. The overall objective is to provide tools for flow prediction that represent accurately the physical mechanism that dominate flow and storage and that are efficient enough that they can be used to design the hundreds of projects at the scale that will be required for widespread application of geologic sequestration.

In the monitoring area, we have completed a scoping study that considered a wide variety on subsurface monitoring methods. From this study, we concluded that seismic is the generic preference for the widest range of storage scenarios, container depths, and geological environments. We next turned our attention to the development of cost-effective seismic-monitoring strategies that could be adapted to changing reservoir conditions. We developed simulation capability involving rock and coal properties with CO$_2$, seismic modeling, and imaging. Our simulation of a simplified model for Sleipner is remarkably similar to the Sleipner field observations. Moreover, we have developed a simulation tool, in diffraction tomography, for rapidly investigating the tradeoffs among imaging issues such as data-acquisition geometry, sampling, signal frequency and signal bandwidth. This rapid simulation capability has been tested but has not yet been used to design or optimize the Adaptive Seismic Monitoring system. This will come in the next phase of the project. Other activities not described in detail above include specific
considerations for monitoring enhanced coal bed methane production (Akintunde, 2004) and the estimation of seismic-attenuation properties for rocks at low seismic frequencies.

Future Plans

In the seal integrity portion of the project in the next months, through the continued collaboration with Dr. Rutqvist, we expect to develop the simulations of CO₂ sequestration for the specific setting like the one we are trying to model in the Powder River Basin. We continue to work on the Ohio River Valley Storage Project, with Amie Lucier working on the project with collaborators at the Schlumberger-Doll Research Laboratory through May. Our geomechanical model and fracture characterization will be complete by mid-summer. Amie Lucier will also work on developing a geomechanical workflow for assessing reservoir suitability using South Eugene Island 330 as a case study during a fall internship at the ExxonMobil Exploration Company.

Work in the area of flow prediction will proceed on several fronts. We will use streamline simulations of aquifer injection to create a suite of initial conditions for a set of high-resolution, high-order finite difference simulations to examine the interplay of heterogeneity, dissolution, gravity segregation of injected CO₂, slow density-driven convection in the brine phase, and diffusion. Those simulations will allow us to judge which simulation tools are appropriate for prediction of what happens in an aquifer after injection has ceased based on the physics of the displacements. We will also continue to develop the physical picture and related simulation tools for coalbeds, and we will continue to investigate experimentally the behavior of multicomponent adsorption of mixed gases in coal.

Future work on monitoring falls into two areas:

(1) Development of specific technology for the assessment and implementation of an adaptive monitoring system. This will include data acquisition, data processing, and analysis and leak-detection procedures. Although we’re focusing our attention on seismic, the lessons learned and procedures developed will apply to other methods (deformation, electromagnetic,…) as well. This effort involves considerable numerical simulation studies, using both the realistic migration toolkit as well as the diffraction tomography toolkit. We anticipate testing our strategies for an adaptive seismic-monitoring system on field data. The final piece of the monitoring strategy we plan to pursue is the analysis and interpretation tools for container assessment and leak detection.

(2) Development of a decision procedure and scoring system for assessing the suitability of a site for monitoring. This process of decision analysis will be similar to the reservoir analysis used to estimate the likelihood of success of 4-D seismic projects in the petroleum industry. It will include site-specific information such as reservoir depth, fluid history, pressure history, rock type, overburden rock, seismic data quality, etc. Of course, however, our scoring system will be based on CO₂ storage issues rather than oil and gas recovery issues.
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Publications
Papers, reports, and theses

Presentations

References
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II.3 Project Results: Geologic CO\textsubscript{2} Sequestration


II.3 Project Results: Geologic CO$_2$ Sequestration


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II.4 Advanced Combustion

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II.4 Introduction to Advanced Combustion

Combustion remains the primary way in which chemical energy is made available for use by humankind. As such, advances in the way that we perform energy conversions using combustion can have a significant impact on the greenhouse gas balance of the planet. Because of its ubiquitous nature, advances in combustion technologies can provide benefits in many areas from home heating, to transportation, to electrical power generation, to industrial processing.

One aspect of combustion that is critical in all arenas is efficiency—the balance between the energy invested to accomplish a task and the work actually required. Efficiency is linked to both how completely the process of combustion can be executed and how well the energy released by the combustion process can be coupled to the energy objective—turning a shaft, cooling a room, etc. In addition to efficiency, it is necessary to achieve combustion in an environmentally sound manner. The potential to produce toxic or photochemically active species during combustion always exists, and insuring that the process is completed within acceptable limits of emissions is critical. Because these two aspects are independent of the fuel used, they are ubiquitous to all combustion systems.

Other aspects of combustion are also generic. The need to understand reaction dynamics (chemical kinetics) and the need to sense chemical species both during combustion and in the post-combustor gases are also requirements of many combustion systems. There are also advanced combustion strategies—for example flameless oxidation—that are not fuel specific and that can be applied to a range of problems when brought to maturity.

Finally there are some fuel-specific combustion technologies that are also critical to success, particularly those that deal with special or exceedingly complex fuels. Hydrogen is an example of a special fuel—a fuel that can be used in unusual ways due to its simplicity. On the other end of the spectrum are biomass and coal. These fuels present significant challenges due to their variable composition, chemical and phase complexities, and potential for forming species that are deleterious to either combustor operation or human health.

In this area of research GCEP has five active projects targeted at specific topics in advanced combustion. The topics of chemical kinetics and sensing are addressed in the work of Profs. Golden and Hanson, respectively. The topic of efficient engine combustion is addressed in the work of Prof. Edwards. Prof. Bowman is pursuing advanced combustion strategies such as flameless oxidation—a form of kinetically controlled combustion. And Prof. Mitchell is pursuing research into the basic mechanisms of biomass and coal combustion—both important fuels for a low greenhouse gas future. Technical summaries of the activities in each of these areas are given below.
II.4.1 Controlled Combustion—An Approach for Reducing Irreversibilities in Energy Conversion

**Investigators**
Craig T. Bowman, Professor, Department of Mechanical Engineering; Neelabh Arora, Kevin Walters, Graduate Research Assistants

**Introduction**
Energy specific CO\(_2\) emissions from combustion devices can be reduced by improvements in energy conversion efficiencies. In conventional combustion devices, the chemical conversion of fuel and air into products occurs rapidly in an unrestrained and highly irreversible process (flame), with work extraction after the completion of combustion. This does not have to be the case. Conversion of fuel and air into products can be accomplished in a more reversible manner if the process is restrained so that work is extracted during the conversion process. An example of work extraction during fuel conversion is the fuel cell. What has not been previously recognized is that the fuel cell is not the only device that has this potential. Using high air preheat and dilute reactants, the chemical conversion process can be slowed to the point where mechanical energy extraction can be used to reduce the irreversibility of the energy conversion process and thereby increase efficiency. One example of controlled combustion is the well-known "flameless" oxidation process\(^1\) in which exhaust heat recovery and exhaust gas recirculation are employed to cause combustion to occur in a more homogeneous fashion. An important additional benefit of this concept is that by controlling the peak temperature of the products, NO\(_x\) emissions can be reduced by orders of magnitude over conventional combustion processes.

In the present project, this concept is being extended to include diluents such as nitrogen and carbon dioxide that could be produced in separation processes and delivered to the combustion system. Carbon dioxide is particularly interesting in that it can have both a thermal and chemical effect on the combustion reaction. The primary objective of the project is to develop and validate detailed models of the combustion chemistry for use in modeling low-irreversibility combustion engine concepts.

**Background**
Figure 1 shows the regimes of combustion processes in terms of the oxygen content of the oxidizer and the preheat temperature. The controlled combustion regime lies outside the regimes of conventional combustion processes as a result of the very low O\(_2\) levels and high preheat temperatures, and the chemical processes in the controlled combustion regime are poorly understood at the fundamental level needed for design optimization, especially for high-pressure combustion systems, such as gas turbines and diesel engines.
II.4 Project Results: Advanced Combustion

![Regimes of combustion](image)

**Figure 1:** Regimes of combustion.

The regime of controlled combustion is being investigated experimentally in a high-pressure flow reactor facility, Fig. 2, in which important parameters, such as preheat and dilution can be independently controlled.

![High-Pressure Flow Reactor (HPFR)](image)

**Figure 2:** High-Pressure Flow Reactor (HPFR)

Figure 3 is a schematic layout of the reactor and the sampling instrumentation.

![HPFR and sampling instrumentation](image)

**Figure 3:** HPFR and sampling instrumentation.
The spatial evolution of the chemical reaction is monitored by sampling for key reactant, intermediate and product species using an extractive sampling probe coupled to on-line analyzers and temperature measured by a thermocouple probe. Detailed modeling of the profile data will yield chemical models for use in the design of controlled combustion systems and particularly for use in modeling low-irreversibility combustion engines, another project being carried out under the Global Climate and Energy Project\(^2\). The starting reaction mechanism is the Gas Research Institute mechanism, GRI-Mech 3.0, for natural gas combustion\(^3\). The fuels being used in the study include methane, ethane and methane-ethane mixtures (to simulate natural gas). The HPFR operates in the pressure range of 1-50 bar. Studies to date have been conducted at atmospheric pressure.

**Results**

Figure 4 show comparisons of calculated profiles of temperature, fuel, CO and CO\(_2\) for methane and ethane at the nominal operating condition of the HPFR, which is in the controlled combustion regime shown in Fig. 1.

![Graphs of temperature and species profiles for CH\(_4\) and C\(_2\)H\(_6\) for an initial mixture temperature of 900°C.](image-url)
II.4  Project Results: Advanced Combustion

As expected, significant differences in fuel reactivity are observed at this operating condition.

Figure 5 shows initial comparisons of calculated and measured temperature profiles at atmospheric pressure for CH$_4$ and C$_2$H$_6$. Good agreement between the model predictions and the experimental data is found.

![Figure 5: Comparison of calculated and measured temperature profiles for CH$_4$ and C$_2$H$_6$ at atmospheric pressure.](image)

**Progress**

The majority of energy forecasts for the 21st century$^4$, $^5$ indicate increased use of fossil fuels to meet global energy demands, particularly in the transportation sector, with a corresponding increase in carbon emissions. Even the most optimistic forecasts$^4$ show significant dependence on fossil fuels for the first half of the century, with a leveling off of carbon emissions by mid century, but at levels that are higher than today. Hence, there can be a beneficial impact on carbon emissions by improvements in the energy conversion efficiencies of combustion-based power systems utilizing fossil fuels. Combining these higher efficiency systems with carbon capture could provide significant benefits in terms of reducing greenhouse gas emissions. The GCEP low-irreversibility combustion engine initiative, of which this project is a part, is investigating this novel approach to reducing irreversibilities through controlled heat release. Given the fundamental nature of this exploratory research effort, it is not possible to estimate the potential for reductions in emissions of greenhouse gases that result from energy use at this time.

**Future Plans**

Over the next year, experiments and modeling in CH$_4$-C$_2$H$_6$ systems will continue. Following completion of the atmospheric-pressure study, higher pressures will be investigated, starting initially at a pressure of 2 bar and then increasing pressure.
References

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II.4.2 Development of Low-Irreversibility Engines

Investigators
C.F. Edwards, Associate Professor, Mechanical Engineering; K.-Y. Teh, S.L. Miller, P.A. Caton, Graduate Researchers

Introduction
In the most general sense of the word, an engine is a device that converts heat or chemical energy into work. The most work that can be developed by a particular engine design is its reversible work. The irreversibility of an engine is the difference between the reversible work that it could develop and the actual work that it performs; it is the lost work. In this research we investigate the potential to design and implement engines with significantly reduced irreversibility, and thereby, improved efficiency.

The relevance of this work to the objective of GCEP is that significant improvements in efficiency are one of the most effective approaches to reducing greenhouse-gas emissions. Since the approach we take is fundamental and comprehensive, it enables improvements both with existing fuels (hydrocarbons) as well as with possible future fuels (e.g. hydrogen).

Background
Improvement of engine efficiency requires efforts in two areas: design and implementation. By design we mean the basic operating cycle or strategy of the engine (e.g., Brayton vs. Stirling cycle). By implementation we mean the degree of perfection with which the design is realized in practice (e.g., the degree to which gas expansion is isentropic). Our focus is on the former (design) aspect. It is based on the realization that current internal combustion engines—gasoline, Diesel, and gas turbine—have been developed based upon an incorrect premise: that they are subject to limitations based on Carnot efficiency. This misconception persists because these engines are often modeled as heat engines (which are subject to Carnot limitations) where, in fact they are reactive engines that are not subject to Carnot proscriptions.

The Carnot misconception has led to erroneous conclusions about how to design combustion engines. The most serious of these is that it is necessary to make the peak temperature in the cycle as high as possible (to improve the Carnot limit). That this is not correct is confirmed by recent experiences with HCCI engines—engines that achieve higher efficiency than their SI counterparts while reducing the peak temperature [1]. And the ultimate example of both the inapplicability of the Carnot criterion and the benefits of low-temperature reaction is the fuel-cell—a reactive engine with first-law efficiency potential in excess of 90% when operated at low temperatures (~80°C for a typical PEM system).

But even before the details of an engine design are considered, it is worth investigating the work potential of the resource that is to be utilized by the engine. This is the available energy or exergy of the resource. The exergy of a chemical resource is found by permitting heat and work to be exchanged between the resource and its environment, and by permitting diffusive and reactive interactions between the two. The reversible work that can be achieved under these most-general conditions is the exergy, and its value is given by the expression...
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\[ X = (U + P_o V - T_o S) - G_o - \Delta G_{r_m} \]

(See reference [2] for a comprehensive discussion of exergy.) This indicates that the absolute upper bound on the work that can be achieved from a resource is dependent upon the both the thermal state of the resource and environment (the first set of terms in parentheses) and on the respective chemical states (the last two terms containing the Gibbs function). For the usual case of a chemical resource that is in thermal and mechanical equilibrium with the environment, it this last term—the change of Gibbs function upon reaction evaluated at the conditions of the environment—that determines its work potential.

Unfortunately, it has proven difficult to construct engines which come close to extracting this limiting amount of work. This is due to a number of complications including the inability to produce perfect devices (turbines, membranes, catalysts) and the inability to produce devices without ancillary complications (e.g., water management in PEM membranes, ionic conductivity in SOFC membranes) that force design choices that are non-optimal (e.g., operation of a fuel cell at elevated temperatures). These later complications often lead to engine designs with what are referred to as option losses—reductions in the reversible work potential from the exergy limit by design. In this case, even if perfect devices are realized to implement the design, the work developed will be less than the exergy limit since the design does not take advantage of all possible interactions with the environment. Analysis of specific designs to determine their reversible-work capabilities is the subject of Second-Law Analysis.

It is in this domain—between the bounds of what is possible from an exergy standpoint and those of conventional engine cycles—that we seek to improve engine performance. Stated another way, we propose to improve reactive engine performance by seeking engine designs that reduce design-associated irreversibility. This is accomplished by branching off from the exergy analysis to include selective interactions between the engine and the environment and to consider how these may be implemented in a mathematically optimal fashion. Note that this is in contrast with second-law analysis which seeks improvements in an existing design by reducing implementation irreversibilities. Here we seek improvements by optimal designs within the limitations of allowed interactions. In short it is our objective to bridge between exergy and second-law analysis to produce new design concepts for engines with minimal option-loss irreversibility.

Results

During this past year, our effort has focused on three aspects of low-irreversibility engines:

1. experimental studies of achieving improved efficiency in piston engines through use of late-phase combustion,
2. computational and analytical studies of adiabatic expansion-engine combustion in order to define optimal design criteria, and
3. analysis of isothermal electrochemical engine (fuel cell) operation in order to develop a counterpart non-electrochemical, isothermal expansion engine.

Each of these topics will be discussed separately below.
Results from Late-Phase Combustion Experiments

Late-phase HCCI combustion shows promise as one means to implement a low-irreversibility engine. The basic premise is that by combining the combustion and expansion processes, energy may be extracted during the combustion process and overall losses may be reduced. This is in some ways analogous to a fuel cell in that since energy is extracted in the process of reaction, peak temperatures are held at much lower values than traditional devices, and entropy generation is correspondingly reduced.

The studies undertaken utilize a single cylinder, variable compression ratio engine equipped with variable valve actuation (VVA) as depicted in Figure 1. The use of VVA permits us to tailor the composition and thermal state of the gases in the cylinder by mixing controlled amounts of hot, burned gases (from the previous combustion cycle) with the fresh air-fuel charge. In doing so, the engine can be made to operate as either a spark-ignition (SI) engine or a homogeneous-charge, compression-ignition (HCCI) engine. Both the engine/VVA system and previous HCCI results are described in detail in reference [1].

The late-phase studies undertaken for this project were performed using optimal conditions as determined from our previous work. Propane was chosen as the fuel so as to provide typical hydrocarbon kinetics but without the possibility of inhomogeneity inherent in liquid fueled engines. It was premixed with the air well ahead (~1 m) of the engine to insure a homogeneous charge. The equivalence ratio was held at 0.95—a value corresponding to optimum operation in our previous tests. Compression ratio was set to 15:1—a value high enough to provide a broad range of HCCI operation but low enough to avoid excessive heat losses.

![Diagram of engine used to study late-phase combustion.](image)

**Figure 1:** Engine used to study late-phase combustion. Closed-loop, fully flexible electrohydraulic valve actuation is used to enable exhaust reinduction for initiating late-phase HCCI. In-cylinder pressure and exhaust emissions are used to determine indicated engine performance metrics.
Two sets of intake valve profiles were used to enact late phase combustion. In this first set, the intake valve was opened at its nominal (SI) opening time, held at full lift, but then closed prematurely (as required to obtain late phasing). In the second set, the intake valve was held open throughout its nominal (SI) period, but the lift was reduced to adjust phasing. In both cases, the exhaust valve was held open throughout the intake stroke (as in our previous studies) so that by adjusting the intake valve alone the residual fraction (mass fraction of burned gas) could be varied.

Figure 2: Effect of residual fraction on phasing of HCCI combustion as indicated by the crank angle at which peak pressure occurs. The black line corresponds to full-lift, partial-duration intake valve profiles. The red line is from full-duration, partial-lift profiles.

As illustrated in Fig. 2, both sets of valve profiles were capable of initiating combustion with phasing after top dead center (ATC). The full-duration, partial-lift strategy was capable of achieving a wider range of residual mass fractions, but the partial-duration, full-lift strategy was able to achieve overall later combustion timings. Note that in either case, increasing the residual fraction causes an increase in the extent to which combustion can be delayed. (Preliminary studies have been conducted which attempt to isolate the effects of late phasing from those of residual fraction, but these are not yet complete and so will be reported at a future date.)

Figure 3 shows the effect of combustion phasing on the indicated thermal efficiency of the cycle. Regardless of the strategy employed, delaying combustion into the expansion process enables a significant increase in efficiency. As phasing is delayed from top center to ~15°ATC efficiency rises from ~30% to ~43%. At a given combustion phasing, some differences due to the choice of valve profiles are evident, but these are generally smaller effects than the overall change with phasing. (The reasons for these differences are currently under investigation.)
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Figure 3: Effect of combustion phasing on indicated thermal efficiency. The black line corresponds to full-lift, partial-duration intake valve profiles. The red line is from full-duration, partial-lift profiles.

Figure 4 shows the effect of combustion phasing on exhaust temperature as measured immediately downstream of the exhaust port. For clarity, only data from the full-lift, partial duration tests are shown. The indicated thermal efficiency is also plotted for comparison. These data indicate that the rise in efficiency does not come at the expense of the exhaust enthalpy. This is consistent with a hypothesis that since the combustion has been delayed, some of the ability to extract energy via expansion work has been lost. The results are inconsistent with the hypothesis that delaying combustion can reduce irreversibility without the occurrence of other effects.

Figure 5 resolves the inconsistencies by showing that the increase in efficiency is due to a drastic reduction in heat losses. Although our objective in studying late-phase combustion has been to reduce combustion irreversibility, these results show that the single biggest effect is to reduce overall heat losses (and their concomitant irreversibility) from the system. This reduction stems from having lowered the peak temperature in the cylinder (by late phasing) such that the driving potential for losses is significantly reduced. An additional component of this reduction may be a reduced convective heat transfer rate due to reduced turbulence (laminarization) during the expansion stroke. Modeling studies of the heat transfer during HCCI combustion are currently underway.

Taken in combination, Figs. 4 and 5 suggest that the potential for improving efficiency via late-phase HCCI combustion is greater than thought previously. This is because the gases have still not undergone optimal expansion. Using VVA, where the compression and expansion ratios can be set independently, the exhaust gases may be expanded further. Studies to investigate the potential of optimal expansion are planned.
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**Figure 4:** Comparison of the effect of combustion phasing on efficiency and exhaust temperature. Only results for full-lift, partial-duration intake valve profiles are shown.

**Figure 5:** Comparison of the effect of combustion phasing on efficiency and heat transfer losses. Only results for full-lift, partial-duration intake valve profiles are shown.
Figure 6 confirms that the reduction of heat loss using late-phase combustion is not peculiar to the full-lift, partial-duration valving strategy. Essentially similar results are obtained with either strategy at a fixed combustion phasing.

![Figure 6: Effect of combustion phasing on heat loss for both sets of valve profiles. The black line corresponds to full-lift, partial-duration intake valve profiles. The red line is from full-duration, partial-lift profiles.](image)

**Results from Simulation and Analysis of Adiabatic Expansion Engines**

In these studies we investigate the possibility of reducing the irreversibility of combustion engines by extracting work during an adiabatic combustion process. The question posed is whether, by suitable choice of the volume-time profile, the combustion and work-extraction (expansion) processes can be combined in an optimal fashion to improve efficiency. In keeping with our ideal design investigations, the analyses are performed assuming an adiabatic enclosure. While the experimental results show that this is not what happens in experiments, this analysis provides a key stepping stone in understanding what is possible in an optimal-design sense. It is also important for understanding what is happening in the engine tests, since in the experiments the effects of heat transfer and reduction of combustion irreversibility cannot be deconvolved. (Analytical studies incorporating the effects of heat transfer are planned for future work.)

**Simulation Procedure**

The simulations are performed using Cantera, an open-source program for chemical kinetics and thermodynamic simulations, in conjunction with the suite of ODE solvers available in MATLAB. The GRI-Mech 3.0 combustion reaction mechanism and its thermochemical database are used in the analysis. Since the combustion mode under
consideration is homogeneous-charge compression ignition, a zero-dimensional model is used; effects of spatial inhomogeneities are not considered.

The process analyzed is based on the slider-crank motion of a reciprocating engine (compression ratio 13:1; ratio of connecting rod length to crank radius 5.52:1) operating at 1800 RPM. Starting with a fuel/oxidizer mixture at bottom dead center (BDC), the compression stroke, carried out adiabatically, raises the mixture temperature and initiates chemical reaction. Under these conditions, a stoichiometric mixture of hydrogen/air diluted by 40% (by mass) of combustion products (water and nitrogen) initially at 425 K, 1 atm is predicted to autoignite at 10°ATC (crank angle degrees after top center). The product gas mixture, at elevated pressure, expands during the power stroke and delivers expansion work to the piston.

To simulate work extraction during the combustion process, the slider-crank motion is modified by varying the speed with which it is executed during the expansion stroke (the compression process remains unchanged). While this motion clearly defies the constraints of real reciprocating engines (as does our assumption of an adiabatic process), it nevertheless provides a simple model by which the feasibility of optimizing combustion via work extraction can be investigated.

Results for Hydrogen-Air Combustion

Figure 7 shows representative pressure and temperature profiles generated from the simulation for increasing piston speed during the expansion stroke. While Fig. 7.a and 7.b show rapid pressure and temperature rises associated with the homogeneous charge combustion model, the peak pressure and temperature decrease with increasing speed of expansion. A higher speed of expansion, corresponding to more rapid work extraction while the combustion is occurring, also leads to a delay in initiation of the combustion process.

Figure 7.c showing pressure and temperature rise near 45°ATC (for an expansion speed of 2288 RPM) is a result of the adiabatic assumption used in the model. The gas mixture temperature remains near 1000 K for an extended period of time while no energy is lost by heat transfer. During this time the pool of reactive radical species is built up instead of depleted, as wall destruction of radicals is not included in the model. The result is the occurrence of combustion far beyond TDC which we would not expect in practice. But this case does help to illustrate the nonlinearity of the combustion process since it depicts how the results change from mild-but-complete combustion at 2288 RPM (Fig. 7.c) to incomplete combustion at 2290 RPM (Fig. 7.d).

Figure 7 shows that work extraction during combustion, by speeding up the expansion stroke of the engine, can partially “restrain” combustion, delaying it and lowering the peak temperature and pressure. However, this is done at the expense of completing the rest of the reaction at a lower temperature and pressure. As a result, the total entropy generated actually increases, as shown on the internal energy-entropy diagram of Fig. 8.

The trend of increasing entropy generation continues until a critical engine speed is attained. Expansion rates beyond this critical speed are too fast for the combustion to go to completion, resulting in a quenched reaction (Fig. 7.d). Consequently, the locus of final $u$, $s$ values for the gas mixture at the end of the power stroke, shown in black in Fig. 8, veers away from the equilibrium product line (red).
Figure 7: Pressure and temperature profiles for dilute H₂/air combustion at four speeds during expansion: a. 900; b. 1800; c. 2288; and d. 2290 RPM respectively.

Figure 8: $u$-$s$ diagram for dilute H₂/air combustion at expansion speeds of a. 900; b. 1800; c. 2288; d. 2288.5; and e. 2290 RPM respectively. The locus of final $u$, $s$ values (black, dotted) shows higher entropy or incomplete combustion when work is extracted during reaction. The lowest entropy generation is for constant-volume combustion.
Besides considering the net amount of work output (which, for an adiabatic system, equals the net difference in internal energy from the start of compression \( u_0 \) to the end of expansion \( u_f \)), an alternative measure of the efficiency of energy utilization is to compare the work output to the exergy decrease during the process. This ratio is termed the *extent of exergy utilization*, and is denoted \( \eta_x \)

\[
\eta_x = \frac{u_0 - u_f}{x_0 - x_f}
\]

A utilization indicates efficient conversion of the exergy to useful work. Figure 9 shows \( \eta_x \) versus \( s \) for the end states of the cases discussed above.

![Figure 9](image)

**Figure 9:** Extent of exergy utilization \( \eta_x \) versus entropy \( s \) for the gas mixture at the end of the expansion stroke. The circles correspond to simulations at the five expansion speeds depicted in Fig. 8.

In Fig. 9 we see that combustion without work extraction remains the most efficient design. Increasing expansion speed reduces \( \eta_x \) until it reaches a minimum at the critical speed discussed above, which corresponds to maximum entropy generation. The lower branch of the \( \eta_x-s \) plot corresponds to rapid expansions that lead to quenched reactions. In this case, some fuel remains after the power stroke and is still available for utilization in a subsequent process. While the net amount of work output is smaller with increasing speed (see Fig. 2), the corresponding amount of exergy destroyed also decreases, leading to higher \( \eta_x \), although it never exceeds the case for slow expansion and near-constant volume combustion.

**Results for Methane-, Propane-, and Methanol-Air Combustion**

Similar results are obtained when, instead of hydrogen, simple hydrocarbons and methanol are used as a fuel. Figure 10 shows the simulation results, summarized on \( u-s \) diagrams, for combustion of methane, propane, and methanol.
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Figure 10: $u$-$s$ diagrams for reaction of a. methane; b. propane; and, c. methanol at several engine expansion speeds, leading to complete, mild-but-complete, and incomplete combustion. The trends are similar to that for hydrogen (c.f. Fig. 8): higher entropy generation and/or incomplete combustion when energy is extracted during reaction.
For each set of simulations, the initial conditions are chosen such that, with the engine operating at 1800 RPM, the fuel/air mixture would autoignite soon after TDC. Unlike hydrogen/air combustion, however, the early part of the compression stroke in hydrocarbon combustion engine is spent in pyrolyzing the fuel, before the oxy-hydrogen reaction mechanism takes over to build up the radical pool for ignition. This delay in ignition can be compensated for by using significantly less dilute fuel/air mixture at higher initial mixture temperature to facilitate thermal decomposition.

The simulations shown on Fig. 10 assume the initial fuel/air mixture is at stoichiometric proportions without dilution. The initial gas pressure is 1 atm. Table 1 lists the initial gas temperatures assumed for the different fuels.

Table 1. Initial gas mixture temperatures used in simulations. Dilution is assumed in H₂/air combustion only.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>( T_0 ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ (diluted by 40% mass of products)</td>
<td>425</td>
</tr>
<tr>
<td>CH₄</td>
<td>525</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>550</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>575</td>
</tr>
</tbody>
</table>

Adiabatic, Reactive Engine Optimization

From the simulation results presented in the previous section, it can be seen that any attempt to extract work while the combustion reaction is underway actually reduces the overall work output of the system. While this conclusion is not comprehensive—it can only be stated as true for the conditions and fuels investigated—it is counter-intuitive and, in fact, opposite to our original, fuel-cell-motivated hypothesis. For this reason, an analytical optimization study was undertaken to test the opposite hypothesis: that for an adiabatic, reactive engine, optimum efficiency occurs when combustion is conducted under constant-volume conditions, regardless of the dynamics of the process. As shown below, this latter hypothesis is correct—one necessary condition for optimal adiabatic combustion is that it occurs at constant (minimum) volume—in agreement with the results of the previous simulations.

The discussion is divided into three sections: the mathematics of constrained system optimization; optimization of the adiabatic, reactive engine system; and the conclusions drawn from the study.

Optimization of Constrained Systems

Consider an autonomous dynamic system whose state \( x: [0, t_f] \rightarrow \mathbb{R}^n \) is described by the ordinary differential equations

\[
\dot{x}_i(t) = f_i(x(t), u(t)), \quad i = 1, \ldots, n
\]

where \( u: [0, t_f] \rightarrow \mathbb{R}^n \) is the input to the system which can be controlled or modified. Given some initial state \( x(0) = x_0 \), prescribing \( u(t) \) as a function of time over the interval \( 0 \leq t \leq t_f \) uniquely determines the evolution of the system over that time interval.

The goal of the optimization process is to modify \( u(t) \) such that the trajectory of system (2) maximizes the functional
subject to various types of constraints. Table 2 lists three types of constraints relevant to the adiabatic piston engine problem at hand.

**Table 2:** Types of constraints in adiabatic piston engine optimization problem.

<table>
<thead>
<tr>
<th>Constraint type</th>
<th>Notation</th>
<th>Eqn.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final state constraints</td>
<td>$x_i(t_f) = (x_f)_i, \quad i = 1, \ldots, p &lt; n$</td>
<td>(4.a)</td>
</tr>
<tr>
<td>Control input inequality constraint</td>
<td>$g(u(t)) \geq 0$</td>
<td>(4.b)</td>
</tr>
<tr>
<td>State inequality constraint</td>
<td>$h(x(t)) \geq 0$</td>
<td>(4.c)</td>
</tr>
</tbody>
</table>

Constraints of the form (4.b,c) place the optimization problem outside the scope of classical calculus of variations. Using topological arguments, Pontryagin *et. al.* [3] derived the Maximum Principle, which provides the necessary optimality conditions for such problems. Alternatively, geometrical concepts such as limiting surfaces can also be used to derive the conditions (see Ref. [4]). Hartl *et. al.* [5] reviewed various forms of the Maximum Principle for problems with state-variable inequality constraints.

One form of the Maximum Principle is presented here in brief, for the specific case of (1) a single input $u: [0, t_f] \rightarrow R$, i.e. $m = 1$, and (2) a single state constraint (4.c) of order 1. This means $u$ explicitly appears after $h(x)$ is differentiated once with respect to $t$.

Constraint (4.c) is assumed active (i.e. $h(x) = 0$) on the time interval $t \in [\tau_1, \tau_2] \subset [0, t_f]$ which is mathematically equivalent to the pair of constraints

$$h(x(u)) = 0 \quad \forall t \in [\tau_1, \tau_2]$$

$$h(x(\tau_2)) = 0$$  \hspace{1cm} (4.c-i) \hspace{1cm} (4.c-ii)

In fact, equation (4.c-ii) can be evaluated at any time $t \in [\tau_1, \tau_2]$ although evaluations at $t = \tau_1$ (the so-called *entry time*) or $\tau_2$ (the *exit time*) are most common.

When constraint $h(x)$ is active, equation (4.c-i) also imposes an additional restriction on the set of admissible inputs originally defined by (4.b). Define this set $\Omega'$

$$\Omega'(x) = \{u : g(u) \geq 0, h(x(u)) = 0 \text{ if } h(x) = 0\}$$

Define the variational Hamiltonian $H$

$$H(x,u,\lambda) = F(x,u) + \sum_k \lambda_k f_k(x,u)$$

where $\lambda_i$ is the co-state corresponding to state $x_i$. The state and co-state dynamics can then be expressed in terms of $H$

$$\dot{x}_i = \frac{\partial H}{\partial \lambda_i}$$

$$\dot{\lambda}_i = -\frac{\partial (H + \nu)}{\partial x_i}$$
where the state constraint (4.c-i) affects the system dynamics via the multiplier $\nu$.

An optimal solution of the problem stated above must satisfy the following necessary conditions (the asterisks denote optimal input, states, and co-states):

$$H(x^*, \lambda^*, u^*) = \sup_{u \in \Omega} H(x^*, \lambda^*, u) = 0 \quad \forall \ t \in [0,t_f]$$ (8.a)

$$\lambda_i^*(t_f) = 0, \quad i = p+1, \ldots, n$$ (8.b)

$$\begin{cases}
\nu = 0 & \text{if } h(x) > 0 \\
\nu \geq 0 & \text{if } h(x) = 0
\end{cases}$$ (8.c)

$$\lambda^*(\tau^-_2) = \lambda^*(\tau^+_2) + \nu(\tau_2) \nabla h(x^*(\tau_2))$$ (8.d)

Equations (8.a) is akin to the Euler-Lagrange equations from calculus of variations. Equation (8.b), a specific form of the transversality condition, means that the co-state $\lambda_i^*$ has to vanish at time $t_f$ unless the corresponding final state $x_i(t_f)$ is prescribed. Equations (8.c,d) impose the constraints (4.c-i,ii). Pontryagin called the discontinuity on co-state trajectories (8.d) an exit jump condition. As discussed above, the equivalent entry jump condition can be derived if (4.c-ii) is evaluated at $t = \tau_1$ instead.

The Maximum Principle as stated above provides necessary optimality conditions without fixing final time $t_f$. The solution for fixed-time problems is readily obtained by introducing a new state $x_{n+1} \equiv t$ with dynamics $\dot{x}_{n+1} = 1$, initial and final state $x_{n+1}(0) = 0$, $x_{n+1}(t_f) = t_f$; the necessary conditions (8.a-d) remain unchanged.

This technique is also applicable to the optimization of non-autonomous systems.

The necessary conditions (8.a-d) result in a multi-point—at times $t = 0$, $t_f$ and one or more exit times $\tau^+_2$’s—boundary value problem involving the ordinary differential equations (7.a,b). One major complication is that the optimal number of switches between constrained and unconstrained system trajectories, as well as the optimal switching times, are not known a priori. Numerical methods based on nonlinear programming are often used to solve for inputs satisfying the necessary conditions of the Maximum Principle (see Ref. [6] for an overview). However, most nonlinear programming techniques are only capable of finding local minima (and maxima) by estimating local gradient and curvature iteratively. Nonlinear constrained optimization in the global sense remains an active area of research.

It is also important to keep in mind that the Maximum Principle is generally not constructive. It provides the necessary conditions that the optimal system input must satisfy. However, an input that is constructed to satisfy all the conditions may turn out to be non-optimal. Sufficiency and uniqueness conditions based on the Maximum Principle often rely on Hamiltonian concavity (see Ref. [5] for details).

**Optimization of Piston Motion for an Adiabatic, Reactive Engine**

In order to understand our experimental and simulation results, the Maximum Principle was applied to the problem of optimizing the piston motion of an adiabatic, chemically reactive engine for maximum expansion-work output. The gas in the cylinder
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is modeled as a homogeneous, ideal-gas mixture. Its thermodynamic state\footnote{In the dynamical system sense, $v$, $Y$ and $T$ are the “states” in this system and will be referred to as such in subsequent sections.} at any time $t$ is defined by the properties:

$v = $ specific volume of the gas, and hence of the piston cylinder;

$Y = $ mass fractions of all $m$ chemical species in the gas mixture (an $m$-vector)\footnote{For each species $i$ ($i = 1, \ldots, m$) $MW_i$ is its molecular weight, while $u_i$ and $c_{vi}$, both functions of $T$, are its total internal energy (chemical plus sensible) and specific heat at constant volume.};

$T = $ gas temperature.

The system dynamics are thus

$$\dot{v} = w$$  \hspace{1cm} (10.a)

$$\dot{Y}_i = f_i(v, Y, T), \quad i = 1, \ldots, m$$ \hspace{1cm} (10.b)

$$\dot{T} = -\frac{RT}{v} \frac{\sum_k MW_k}{\sum_k c_{vi} Y_k} \frac{w}{v} + \frac{\sum_k u_k f_k}{\sum_k c_{vi} Y_k} = f_T(v, Y, T, w)$$ \hspace{1cm} (10.c)

Cast as an optimization problem as presented in the previous section, the functional to be maximize is

$$\int_{t_0}^{t_f} RT \frac{\sum_k MW_k}{\sum_k c_{vi} Y_k} \cdot w \, dt$$  \hspace{1cm} (11)

The input to the system, $w$, is the rate of volume change for the gas and is taken to be directly proportional to the piston speed (10.a). Chemical kinetics dictate the net production rate of species $i$, denoted $f_i$ (10.b). For gas-phase reactions due to molecular collisions, $f_i$ is solely a function of the states. Conservation of energy for the adiabatic system then determines the rate of change of the gas temperature, denoted $f_T$ (10.c). $f_T$ depends on the states, but is also a linear function of the input $w$.

The system is constrained as follows: (1) The time of reaction $t_f$ is fixed. The technique of introducing a new state $\tau \equiv t$ will be used to address this constraint. (2) All initial states are prescribed, with the cylinder restored to its initial volume at time $t_f$.

$$v(0) = v_0$$

$$v(t_f) = v_0$$

$$Y(0) = Y_0$$

$$T(0) = T_0$$ \hspace{1cm} (12.a)

(3) The piston speed is bounded by the (common) maximum compression and expansion speed $w_m$. Imposing this input constraint makes physical sense, and is also essential for the analytical results below.

$$|w| \leq w_m$$ \hspace{1cm} (12.b)
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(4) The geometric compression ratio of the engine is fixed at $CR$. The inequality $v_0 CR \leq v \leq v_0$ is expressed as two state inequality constraints of the form (4.c)

$$
\begin{align*}
    h_{TC}(v,Y,T) &= v - v_0 / CR \geq 0 \\
    h_{BC}(v,Y,T) &= v_0 - v \geq 0
\end{align*}
$$

(12.c)

For this piston engine optimization problem, the Hamiltonian $H$ is linear with respect to the input $w$.

$$
H = Pw + \lambda_v w + \sum_k \lambda_k f_k + \lambda_T f_T + \lambda_T
$$

$$
= \left[ RT \sum_k \frac{Y_k}{MW_k}(1 - \frac{\lambda_T}{\sum_k c_{v_k} Y_k}) + \lambda_v \right] \cdot \left[ \sum_k \lambda_k f_k - \lambda_T \sum_k u_k f_k \right] + \lambda_T
$$

$$
= H_1(v,Y,T) \cdot w + H_2(v,Y,T)
$$

(13)

where the restricted set of admissible input is

$$
\Omega' = \{ w : |w| \leq w_m, \text{ and } w = 0 \text{ if } v = v_0 / CR \text{ or } v_0 \}
$$

(14)

By Equation (8.a) of the Maximum Principle, the optimal input $w^*$ must maximize $H$. Therefore, $w^*$ can only take on one of three values at any instant $t \in [0, t_f]$:

$$
\begin{align*}
    w^*(t) = \arg \sup_{w \in \Omega'} H = \begin{cases}
        +w_m & \text{if } H_1 > 0, h_{TC,BC} \text{ inactive} \\
        -w_m & \text{if } H_1 < 0, h_{TC,BC} \text{ inactive} \\
        0 & \text{if } h_{TC} = 0 \text{ or } h_{BC} = 0
    \end{cases}
\end{align*}
$$

(15)

In other words, the optimal piston motion that maximizes the expansion work output is piecewise constant. The piston moves at either maximum compression or expansion speed, depending on the coefficient $H_1$ of the Hamiltonian (13), unless the piston is constrained by the geometric compression ratio of the engine, in which case it remains stationary at TDC or BDC.

Conclusions from this Study

As shown via the Maximum Principle, any piston motion that is not piecewise constant—for instance, the slider-crank motion—does not maximize the expansion work output for an adiabatic, reactive engine. Optimally, the piston would move at either maximum compression or expansion speed, or remain stationary when at TDC or BDC. This is consistent with the simulation results presented above, which indicate that work output of the engine is highest when combustion is allowed to proceed at constant volume near TDC without attempting to extract work during the reaction process. We therefore conclude that adiabatic, constant volume combustion at the minimum allowable volume is likely to maximize the piston work output.

Equally important is the observation that changing the gas phase chemical kinetics would not affect this conclusion, as the Hamiltonian $H$ remains linear with respect to input $w$ (i.e. piston speed). The structure of $H$ changes only if the adiabatic assumption on the system model is abandoned. This is an important and counter-intuitive conclusion.
In effect we have proven that for the overly restrictive adiabatic, reactive expansion case, regardless of dynamics, the optimal solution cannot be obtained by contouring the volume-time profile alone. We also note that the opposite is true—for the less restrictive case with a specified non-linear interaction, we expect that an optimal, non-limit-value solution for the volume-time profile will exist. Understanding that optimization problem—in particular the case permitting heat transfer—is one of the next topics that will be addressed in this research.

Results from Analysis of Isothermal Electrochemical and Expansion Engines

Fuel cells are isothermal electrochemical engines that convert chemical energy stored in the bonds of a fuel into electrical work. A PEM (Proton Exchange Membrane) fuel cell uses hydrogen and oxygen as fuel. For every hydrogen molecule consumed, two electrons travel across a potential gradient from the anode to the cathode, producing electrical work. Other work producing devices, specifically combustion engines, first convert chemical energy into sensible energy, raising the overall entropy of the system and therefore, decreasing the theoretical work output. The expansion analogue to the fuel cell, an isothermal device that converts chemical energy directly into a pressure gradient, should have higher theoretical efficiencies than current combustion engines. Our objective in this work is to see if such a reversible expansion engine can be developed.

To understand how this expansion device would work, the fuel cell must be analyzed more closely. A diagram of a PEM fuel cell is shown in Fig. 11. It is composed of two electrodes, each coated with a platinum catalyst surrounding a polymer electrolyte. In a PEM fuel cell, H₂ undergoes dissociative chemisorption onto the platinum catalyst. The electron is pulled into the conduction band by the ionic cores of the platinum, allowing the proton H⁺ to enter the electrolyte. The proton diffuses across the electrolytic semipermeable membrane due to a concentration gradient until it reaches the cathode. At the cathode, the protons combine with the oxygen that is adsorbed onto the cathode’s platinum surface.

![PEM Fuel Cell Diagram](image-url)

**PEM Fuel Cell Reaction**

Anode: \( \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \)

Cathode: \( 2\text{H}^+ + 2e^- + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \)

Total: \( \text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \)

**Figure 11:** PEM Fuel Cell Diagram. H₂ and O₂ react isothermally to form H₂O by directly converting chemical energy into an electrical potential.

The cathode is now at a higher voltage than the anode, creating a positive electrical potential for the electron at the anode. The electron moves to the cathode through its own semipermeable membrane, the conduction band of the metal catalyst and external wiring,
to combine with the proton and oxygen. The water that is formed is drained from the catalyst to maintain the concentration gradients for the reactants. Electrical work is extracted from the electron as it moves across the electrical potential gradient. This work is proportional to the cell potential difference

$$W_{\text{out}, \text{max}} = -\Delta G_{\text{tot}} = -\Delta \mu_{\text{tot}} = \mu_{\text{H}_2} + \frac{1}{2} \mu_{\text{O}_2} - \mu_{\text{H}_2\text{O}} = 2F(\varphi_{\text{cathode}} - \varphi_{\text{anode}})$$

where $W_{\text{out}, \text{max}}$ is the maximum work output per mole of $\text{H}_2$ and $G$ is the molar Gibbs free energy which is equal to $\mu$, the chemical potential, $F$ is Faraday’s constant, and $\varphi$ is the electrical potential. The two in the last term is required because two moles of electrons flow for every mole of hydrogen consumed. The maximum possible work coincides with the maximum cell potential and occurs theoretically at equilibrium.

An abstract version of the fuel cell diagram is shown in Fig. 12 below next to a similar diagram of the expansion device analogue. Species $\text{AB}$ and $\text{C}$ are the reactants and enter the device separately at points labeled (1) and (2) on the diagram. These labels replace the “anode” and “cathode” labels on the fuel cell diagram. Specie $\text{AB}$ enters the system at (1) and splits into its components $\text{A}$ and $\text{B}$. Specie $\text{A}$ diffuses to (2) through a semipermeable membrane creating a partial pressure increase in $\text{B}$ at (1). Specie $\text{B}$ then flows to (2) where it combines with $\text{C}$ and $\text{A}$ to form the product $\text{ABC}$. In this device the work is extracted from a pressure gradient rather than an electrical potential gradient. Since specie $\text{A}$ is diffusing due to a chemical gradient, it might be possible to extract work here as well as from the flow of specie $\text{B}$. The analogy with the fuel cell is consistent with this idea; if a device existed that could extract work from the flow of protons across the electrolyte, work could be extracted in this manner from fuel cells too.

At equilibrium, $\Delta G_{\text{tot}} = \Delta \mu_{\text{tot}} = 0$ at both points (1) and (2) on the device.

$$\Delta \mu_1 = \mu_A + \mu_{\text{B1}} - \mu_{\text{AB}} = 0; \text{ and}$$

$$\Delta \mu_2 = \mu_{\text{ABC}} - \mu_A - \mu_{\text{B2}} - \mu_C = 0$$

where $\mu_i$ is the chemical potential of specie $i$. The chemical potential can be written to show its dependence on the partial pressure of specie $i$

$$\mu_i = \mu_i^0(T,P_i^0) + RT\ln(P_i/P_i^0)$$

where $R$ is the universal gas constant, $T$ is the temperature, $P_i^0$ is the reference pressure and $P_i$ is the partial pressure of specie $i$. Assuming, as in the fuel cell, that there is no work extraction from the diffusion of specie $\text{A}$, at equilibrium the partial pressure of specie $\text{A}$ is a constant everywhere. Only specie $\text{B}$ has a partial pressure difference from (1) to (2). Adding $\Delta \mu_1$ and $\Delta \mu_2$ together and solving for $\Delta \mu_{\text{overall}}$ ($W_{\text{max}}$) shows that the maximum work is proportional to the pressure gradient of specie $\text{B}$ at constant temperature

$$\Delta \mu_1 + \Delta \mu_2 = \Delta \mu_{\text{tot}} = 0 = \mu_{\text{B1}} - \mu_{\text{AB}} + \mu_{\text{ABC}} - \mu_{\text{B2}} - \mu_C$$

$$\mu_{\text{ABC}} - \mu_{\text{AB}} - \mu_C = \mu_{\text{B2}} - \mu_{\text{B1}} = RT\ln(P_{\text{B2}}/P_{\text{B1}}) \text{ at constant } T$$

$$W_{\text{out}, \text{max}} = -\Delta \mu_{\text{tot}} = -RT\ln(P_{\text{B2}}/P_{\text{B1}}) \text{ at constant } T$$

The maximum work possible for an isothermal system (like the fuel cell) is based on the difference in partial pressures between (1) and (2). (Note that $P_{\text{B2}} < P_{\text{B1}}$ so that the $W_{\text{out}}$ is positive.)
A better thermodynamic understanding of the fuel cell will potentially help in designing this expansion work device. The electrochemical potential is a useful property for describing a fuel cell, combining the chemical potential of a species with its electrical potential. Since a fuel cell is a constant temperature and pressure device, the chemical and electrical potentials are the only two driving gradients. The electrochemical potential is defined as

\[ \mu_{\text{bar},i} = \mu_i(T, P_i) + z_i F \phi \]

where \( \mu_i \) is the chemical potential of specie \( i \) at \( T \) and \( P_i \), \( z_i \) is the species charge, \( F \) is Faraday’s constant, and \( \phi \) is the electrical potential. Since \( z_i \) must be nonzero for the second term to contribute, only charged species have an electrical component. For uncharged species such as \( \text{H}_2 \), \( \mu_{\text{bar,}H_2} = \mu_{\text{H}_2} \).

Knowing the chemical and electrical potential of each species in the fuel cell will give more information about how the fuel cell converts chemical energy directly to electrical energy. At equilibrium, the total change in electrochemical potential is equal to zero at both the anode and the cathode. The chemical reaction at the anode is \( \text{H}_2(\text{g}) \rightarrow 2\text{H}^+(\text{aq}) + 2e^-(\text{Pt}) \) which can be used to write an equation for the total change in electrochemical potential at the anode

\[ \Delta \mu_{\text{bar}} = 2\mu_{\text{bar,H}^+(\text{aq})} + 2\mu_{\text{bar,e}-(\text{Pt})} - \mu_{\text{bar,H}_2(\text{g})} = 0 \]

Substituting the definition of \( \mu_{\text{bar}} \) and rearranging

\[ -2\mu_{\text{H}^+(\text{aq})} - 2\mu_{e-(\text{Pt})} + \mu_{\text{H}_2(\text{g})} = 2F(\phi_S - \phi_A) \]
where $\phi_s$ is the potential of the solution and $\phi_A$ is the potential of the anode electrode. A similar balance for the cathode reaction ($2\text{H}^+(aq) + 2e^-(\text{Pt}) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}$) yields

$$-\mu_{\text{H}_2\text{O}} + 2\mu_{\text{H}^+} + 2\mu_{e^-} + 0.5\mu_{\text{O}_2} = 2F(\phi_C - \phi_S)$$

where $\phi_C$ is the potential at the cathode.

Determining the chemical potential of each species, arbitrarily setting $\phi_A$ equal to 0, and solving for $\phi_S$ and $\phi_C$ provides all the information needed to solve for the electrochemical potentials of each species. $\text{H}_2(g)$, $\text{O}_2(g)$, and $e^-(g)$ at 298 K are chosen as reference species. Entropy is zero at zero Kelvin. Figure 13 is a plot of $\mu_i$, the chemical potential vs. $\phi_i$, the electrical potential for each species. The virtual state for a species represents the magnitude of its total potential; all of the species’ electrical potential has been converted to chemical potential. The figure tracks the energy transfers starting with one molecule of $\text{H}_2$ and $\frac{1}{2}$ molecule of $\text{O}_2$ which is why it is necessary to plot 2 protons and 2 electrons. The units for the figure are electron Volts (eV) which are easily converted to a cell potential by dividing by the number of charges. For instance, the two electrons at the cathode have an electrical potential of 2.46 eV which equals the familiar 1.23 V cell potential for a PEM fuel cell.

**Figure 13:** Chemical Potential ($\mu$) vs. Electrical Potential ($\phi$) for a PEM fuel cell at equilibrium conditions.
Hydrogen enters the system and is split into low chemical potential electrons and high chemical potential protons. The total electrochemical potential of the protons (shown by the virtual state) is lower than the proton chemical potential because the protons have moved to a lower electrical potential in the solution. The protons’ electrochemical potential is the same across the entire membrane at equilibrium. The electrons’ chemical potential is the same at the anode and the cathode since the electrons are always in the conduction band of the platinum. Their electrical potential changes, however, as they move down an electrical gradient to the positively charged cathode. The virtual state for the electrons shows that their lowest potential energy is at the cathode. Work, denoted \( w \), is extracted from the electron motion. At the cathode, the protons, electrons, and oxygen combine to form the final product, water.

A similar figure can be made for the expansion work device, where the axes would be chemical potential vs. partial pressure. By mapping the fuel cell energy transfers, we hope to identify the requirements necessary to make the analogous expansion work device—potentially a reversible expansion engine. Efforts to that end are currently under way.

**Progress**

The last year has seen significant progress toward defining what is possible in the development of low-irreversibility engines. During the first year of the project, preliminary simulations were performed and possible experimental approaches were assessed. During this second year, we selected the piston-engine system as the experimental focus of our studies and initiated specific efforts to understand and prove what is possible in developing improved engine designs. In the experimental work, we have been able to demonstrate that late-phase combustion can lead to significant improvements in efficiency—as hypothesized—but that this improvement is most likely due to a decrease in heat transfer and not a reduction in combustion irreversibility. At the same time, we have also identified that further significant gains are likely to be possible since the working fluid remains highly energetic.

The observation about the mechanism of efficiency improvement in the experiments was bolstered by numerical simulations for adiabatic combustion with expansion. These showed that for a particular family of expansion profiles and fuels, completion of combustion at minimum volume always gave the highest efficiency (and lowest combustion irreversibility). Perhaps the most important accomplishment this year is the extension and application of the Maximum Principle to this optimal adiabatic, expansion problem. The importance of this result is that it shows that regardless of the dynamics of the system (i.e., the chemical kinetics) the necessary condition for an optimal solution to this problem requires that combustion occurs either at maximum or minimum or zero piston speed. Stated another way, because of the linear dependence of the work output on expansion rate, an extremum in the solution can only occur at the extreme design points of expansion rate. From both experiments and simulations, it appears likely that the optimal solution occurs with zero expansion during combustion, that is, at constant volume. Again, the importance of this proof is that it removes the requirement to search the space of possible dynamics—as was initially done in our numerical simulations.
The other benefit of this proof is that it brings into focus what is required to find an optimal design. That is, a non-linear energy interaction. The most obvious of these is heat transfer, which will be the next step in our analytical work. This step will also bring our analysis work into line with our experimental observations. Moving in this direction is also consistent with our objective to systematically explore the space of optimal design as successive interactions are admitted in the design space.

The other area where significant progress has been made is in exploration of whether it is possible to develop an expansion engine that embodies the low-temperature, high-efficiency attributes of the fuel cell (but with using electrochemical work). Having identified a suitable way to extract energy from the chemical potential of the reactants—adiabatic expansion—we have analyzed the energy processes of the PEM fuel cell system in order to better understand what will be required in the design of such an expansion engine. This has been a challenging exercise—certain characteristics of fuel cells that one might believe would be well known, and that are critical to the type of reverse-engineering approach that we have taken, have turned out to not be known. This is less surprising in hindsight, since these are detailed questions which are not often asked except for the most fundamental reasons. But having resolved these questions, the construction of the chemical-potential/electrical-potential diagram shown in the text is a key step towards understanding how a reversible expansion engine might be designed. Because this is a novel idea with a very high efficiency potential, that goal remains a key stretch target of our research in the next year.

**Future Plans**

A number of research efforts have been identified throughout the discussion and are currently underway. These include:

1. Experiments to expand the range of late-phase HCCI operation and to explore optimal expansion to further increase efficiency.
2. Incorporating the effect of heat transfer in the simulation model and the dynamic system analysis used for optimization.
3. Investigating the option of allowing heat transfer within the system boundary (i.e. regeneration) in a low-irreversibility reactive engine.
4. Refining electrochemical potential estimates for the PEM fuel cell, including effects such as hydrogen adsorption on platinum and proton concentration in the membrane.
5. Estimating heat transfer and activation energies to better understand the role of the metal catalyst in the PEM fuel cell. This understanding will help in defining the required characteristics for a reversible expansion engine.

**References**

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II.4.3 Sensors for Advanced Combustion Systems

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Introduction
The objective of our research has been the development of advanced sensors that have the potential to: (1) minimize the environmental impact of energy conversion via control of combustion-generated pollutants such as NO, CO and unburned hydrocarbons; (2) reduce greenhouse gas (CO2) by improving combustion efficiency; and (3) monitor the fugitive emissions from greenhouse gas sequestration efforts. These novel sensors should enable a new generation of strategies for active monitoring and control of combustion and energy conversion technologies of the future.

During the past year, multiple new sensor strategies have been developed and demonstrated, all based on tunable near-infrared (NIR) diode lasers and absorption spectroscopy. Our longterm goal is to incorporate this new sensor technology into closed-loop control strategies to maximize combustion efficiency and/or minimize key emissions (UHC, CO, and NO). Eventually these sensors should enable active combustion control strategies to suppress combustion instabilities for advanced combustor development.

Our research has focused on three sensor technologies: 1) a robust, rapid-response gas temperature sensor using fiber-coupled laser technology and a combination of scanned-wavelength and wavelength-modulation strategies; 2) a fiber-coupled, wavelength-multiplexed sensor for gas temperature, O2 and CO suitable for monitoring large-scale coal combustors; and 3) novel fuel sensing strategies for the sensitive detection of unburned hydrocarbons in combustor exhaust and for fast, robust sensing of hydrocarbon fuels as needed for active combustion control of instabilities. These sensors thus offer great promise for monitoring and control of combustion and energy conversion technologies of the future.

Background
Efficiency improvements in large-scale combustors can produce immediate benefits. First, savings on the order of $1M/year in coal accrue for an average 600 MW boiler with an efficiency increase of only 1% with a simultaneous reduction in CO2 emissions. In the near future, one can envision that CO2 credit arbitrage will become the norm just as NOx credit trading occurs today. Second, efficiency improvement can also reduce NOx emissions, enabling a utility to sell NO credits or avoid expenditures for pollution-control equipment. For the average 600 MW boiler, a 20% NO reduction amounts to elimination of 1800 tons per year of NOx, which is valued near $4,500,000 at a typical NOx credit price (varies by state and year). Third, efficiency improvement via complete combustion could improve some of the deleterious conditions that can occur in boilers such as...
slagging and corrosion, and these improvements will ultimately reduce maintenance costs.

Coal-fired boilers are routinely only tuned or optimized at monthly or sometimes even yearly intervals rather than on a continual basis. There are many reasons for this laissez faire situation including a lack of sensors to provide useful information for feedback into the optimization process, antiquated equipment, and a general ambivalence on the part of some utilities. However, this state of affairs is beginning to change. A few companies have developed optimization software that takes current sensor inputs from diverse sources such as oxygen sensors, CEMs measuring pollutants, airflow measurements, and coal loading measurements and optimizes the combustion process. Improvements on the order of 0.5 - 1% for heat rate and 20% NO reduction are routinely attained. However, all information regarding combustion efficiency currently comes from sensors placed well downstream of the boiler. Often these sensors are extractive, which can lead to serious measurement errors if great care is not taken in their installation. One expects that better measurements could be made if sensors were available that would measure combustion parameters directly in the combustion zone without extractive probes. Clearly this presents a challenge due to the extremely hostile environment of the boiler. Optical diagnostics have a significant advantage in this regard since no intrusive probes are required.

Laser-based sensors are in-situ, non-intrusive devices, which remotely interrogate the reactive gas/liquid stream and avoid the problems of wall-mounted or extractive sampling sensors in common use. These modern sensors, based on absorption spectroscopy, target specific chemical components and/or local temperature and thus enable novel new control strategies for a wide range of applications.

Tunable diode laser (TDL) spectroscopy for combustion diagnostics have been developed over the past 20 years by a variety of practitioners with much of the pioneering effort performed in our laboratory at Stanford University. Although the majority of this work was done in well-controlled, laboratory-scaled flames, there are some notable exceptions.[1] At Stanford, Furlong et al. performed the first-ever closed loop combustion control with laser sensing. They utilized a wavelength-multiplexed TDL sensor of gas temperature and adaptive control to reduce the CO and unburned hydrocarbon emissions from a 50kW incinerator by more than an order of magnitude.[2] Recently in Germany, Teichert et al. demonstrated quantitative detection of CO, H₂O concentration and temperature in a coal-fired utility boiler using a multiplexed-wavelength laser sensor,[3] although no effort was made at combustion control. Similarly, in Japan, Deguchi et al. measured CO and O₂ concentration in a waste incinerator.[4] Finally, our research group at Stanford has demonstrated quantitative species detection and temperature measurement in a variety of realistic aerospace combustion applications including pulse detonation engines, SCRAMJET combustors, and gas turbine combustor sector test rig using multiplexed wavelength laser sensors.[5,6]
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Results
During the past year, we have made significant progress on three different TDL sensor technologies, all with good potential for combustion control applications: 1) a rapid response gas temperature sensor, 2) a fiber-coupled, wavelength-multiplexed sensor for gas temperature, O2, and CO suitable to monitor large-scale coal combustors, and 3) novel fuel-sensing strategies.

a. Rapid-response gas temperature sensor
A diode-laser sensor system has been developed for non-intrusive measurements of gas temperature in combustion systems using a combined scanned-wavelength and wavelength-modulated strategy with 2f detection. The sensor is based on a single diode laser (distributed-feedback), operating near 1.4 microns and scanned over a spectral range targeting a pair of H2O ro-vibrational transitions. The single-fiber-coupled-laser design makes the system compact, rugged, low cost and simple to operate. Gas temperature is inferred from the ratio of the second harmonic signal of two selected H2O transitions.[7] The sensor design includes software for fast data acquisition and analysis to provide rapid temperature measurements, and a temperature readout rate of 2.5 kHz has been demonstrated for measurements in a C2H4/air laboratory flame at atmospheric pressure. The combination of scanned-wavelength and wavelength-modulation avoids interference from emission and provides a robust temperature measurement that is useful for combustion control applications.

Water is a primary combustion product and its prevailing and relatively strong absorption spectra in the near-infrared region make it an ideal species for temperature measurement. By suitable choice of laser wavelength it is possible to measure temperature using a single diode laser. The use of a single diode laser greatly simplifies the sensor system and reduces cost compared with wavelength-multiplexing techniques developed previously in our laboratory.

In an earlier study we showed that temperature inferred from water vapor is a good control variable for complete combustion and reduced emissions in a forced vortex incinerator [2]. Optimal selection of specific water vapor absorption features is an important step in sensor design. Figure 1 shows a segment of the calculated H2O (10%) spectra near 1.4 µm based on HITRAN parameters and a pressure of 1 atmosphere. This pair of features (7154.354cm^-1 & 7153.748 cm^-1) is selected for several reasons. Most importantly, both features are well resolved at one atmosphere pressure avoiding interference by neighboring transitions, and both features have similar absorption coefficients and thus will have similar measurement uncertainty. Additionally, these two features have sufficiently different lower state energy E” to yield a high temperature sensitivity; the E” values of 1789 cm^-1 and 2552 cm^-1 insure that the transitions will be strongest at temperatures much larger than room temperature while their relatively weak absorption at room temperature minimizes interference from ambient air in the measurement path. The selection of these two transitions offers the opportunity to simplify the equipment needed for a practical combustion temperature sensor.
It was necessary in our research to measure the needed spectroscopic parameters in a heated cell (including line strengths, line center frequencies, broadening coefficients and lower state energies). Discrepancies were found between our measured quantities and the database known as HITRAN, hence our research has already yielded important contributions toward an accurate scientific database for water vapor spectroscopy.

Though the 2f peak height depends on many parameters such as linestrength, mole fraction, pressure, laser intensity, and lock-in settings, etc., the 2f peak ratio of two transitions can be made equal to the linestrength ratio by optimizing modulation depths. [7] Example results confirming the accuracy of this proposed method are shown in Fig. 2. Note that the individual data points, obtained with different values of 2f modulation depths (denoted by ‘a’) agree very closely with the simple linestrength ratio.

**Figure 1**: Calculated spectroscopic features for water (10%) line pair near 1.4μm based on HITRAN parameters.

**Figure 2**: Normalized 2f peak ratio versus temperature.
Figure 3 illustrates the general arrangement of experimental setup for the 2f- single-laser sensor. Light from the DFB diode laser is coupled into a single optical fiber and directed across the Hencken laboratory burner. The wavelength of the laser is scanned across the spectral region of interest at a repetition rate of 2.5 kHz; superimposed on this is a small modulation at f=100 kHz. The ratio of the absorbance for the two water vapor absorptions provides 2.5 kHz temperature measurements. Comustion instabilities can be identified from the gas temperature measurement. Temperature fluctuations in the Hencken burner are induced by modulating fuel flow through a speaker to mimic the expected response from combustion instability. The Fourier transform of a time series of gas temperature clearly identifies the dominant and harmonic modes of the temperature fluctuations. The results obtained demonstrate the utility of this sensor for quantitative, accurate identification of temperature fluctuations needed for combustion control.

Figure 3: Schematic of diode laser based T sensor in a laboratory flame.

b. Wavelength-multiplexed TDL sensor for T, H₂O, O₂, and CO in large-scale combustors for electric power generation

We have teamed with Zolo Technologies to design a wavelength-multiplexed diode laser sensor for application in a coal-fired electric utility combustor. A wavelength-multiplexed sensor using optical fiber technology allows the lasers, control electronics, detectors, and data acquisition to be remotely located in the control room of the utility far from the harsh environment of the combustor. The fiber-based sensor is possible because of a unique wavelength-multiplexer technology developed by Zolo Technology for the telecommunications industry. The sensor illustrated in Fig. 4 combines light from five individual diode lasers into a single fiber for delivery to the combustor. The transmitted light is collected into a multimode fiber and returned to the control room where a second Zolo device disperses the light onto separate detectors. Each beam monitors the absorption on a different segment of the spectrum. Light near 760nm is used to monitor oxygen, near 1559 nm for carbon monoxide, and three regions between 1350 and 1400 nm are used to monitor multiple absorption features in water vapor. Temperature is determined by ratios of the water vapor absorption. In addition to the lasers, the
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demonstration sensor shown in Fig. 4 included a multiplexer, transmission optics, receiver optics, a demultiplexer, detectors, and a signal digitization and processing system. The switch allows the beam to serially probe multiple spatial locations using the same laser source and detection system.

![Diagram of wavelength-multiplexed TDL sensor](image)

**Figure 4:** Schematic diagram of wavelength-multiplexed TDL sensor using a Zolo Technologies multiplexer/demultiplexer.

A preliminary measurement campaign was conducted with this prototype Zolo/Stanford sensor at the Valmont Station, Boulder, Colorado coal-fired electric utility. The tangentially fired boiler ran at full load burning Powder River Basin (PRB) coal and produces 220 MW of electricity. Two measurement positions were located ~ 10 meters and ~ 13 meters above the coal injectors. In spite of significant transmission losses due to obscuration by coal dust and fly ash (average transmission = 1–5x10^-4 ten meters above the coal injectors over a 1.5 meter path), we were able to measure temperature and monitor the target species with a typical signal to noise shown in Fig. 5. Several such scans in multiple wavelength regions are analyzed to determine temperature.

![Absorbance vs Wavenumber](image)

**Figure 5:** Experimental wavelength scan encompassing several water absorption features in the 1376 nm spectral region.
This work represents several notable accomplishments including the first use of an all-fiber-coupled device for measurements on a coal-fired boiler and the first simultaneous detection of three species (CO, H$_2$O, and O$_2$) and temperature in a coal-fired utility boiler. The good signal-to-noise illustrated in Fig. 5 can be collected on each laser channel in less than 100 ms; and high quality operation point control signals can be reported at 3 second intervals. This measurement bandwidth is much faster than any actuation strategies for a combustor of this size. Thus, this sensor offers excellent potential to as part of a control system for closed-loop optimization of the power plant combustor.

c. Fuel sensor development

Modern combustion control strategies require fuel sensors for two different applications: 1) sensitive detection of unburned hydrocarbons in the combustor exhaust and 2) measurement of local fuel/air stoichiometry in the combustor. Although the smallest fuel molecules CH$_4$, C$_2$H$_2$, and C$_2$H$_4$ have rotationally-resolved (or near-rotationally-resolved) spectra at one atmosphere, optical detection of most hydrocarbon fuels is complicated by the broad, unstructured infrared absorption spectrum as illustrated in Fig. 6. Therefore, the sensing of fuel is not as well developed as is the sensing of O$_2$, CO, or H$_2$O. During the past year, we have investigated the potential for detection of C$_2$H$_4$ and C$_3$H$_8$ using tunable near-infrared laser light, and fixed-wavelength absorption in the mid-infrared for a variety of practical fuels.

![Figure 6: Example absorption spectra for hydrocarbon fuels.](image-url)
The mid-infrared does not have the robust, inexpensive laser and fiber technology available in the near infrared. Therefore our choices are limited to available fixed wavelength lasers. The HeNe laser at 3.39 μm is readily available and provides a stable laser source to investigate sensitive strategies for hydrocarbon fuel detection. During the past year we have built a heated flow cell with mid-infrared optical access to quantify the temperature dependence of the 3.39 μm absorption coefficient over the range of temperatures expected in a variety of practical propulsion combustors.

![Graph](image)

**Figure 7:** Segment of the C2H4 spectrum in the NIR at atmospheric pressure.

The near-infrared absorption of C2H4 provides an opportunity to develop TDL sensors for fuel to test control strategies in the anticipation of new mid-infrared laser sources for practical fuels. During the past year we have investigated a novel differential absorption strategy to measure C2H4 fuel concentrations, and Fig. 7 shows the segment of the C2H4 spectrum used. We are now prepared to monitor C2H4 in a swirl-stabilized laboratory flame.

**Progress**

Good progress has been made toward development of a new class of combustion sensor, based on TDL absorption spectroscopy, for active and operating point combustion control. Scanned-wavelength and wavelength-multiplexed sensors have advanced to a stage of readiness for combustion control demonstrations. Exploratory measurements in a large-scale coal fired power plant suggest that efficiency improvements of 1-3% may be feasible with simultaneous reductions in CO2 and NOx emissions. The economic and environmental consequences of such improvements are very large.

Control of combustion using feedback from advanced fast-response sensors has the potential to minimize the environmental impact of energy conversion; for example, lean, premixed firing of gas turbines can significantly reduce NOx emissions. However, lean, premixed flames are sensitive to instabilities and prone to flame blow-out or flashback. Active combustion control of the pressure fluctuations leading to these failures could decrease the current large safety margin and thereby reduce the flame emissions. Similarly, emissions from coal-fired utility boilers are the focus of increasing scrutiny. Early emphasis on reduced emissions of NOx and SOx is now being coupled with a desire to reduce CO2 emissions. These goals can be simultaneously achieved by improving the efficiency of the combustion process in the boiler. In general, coal-fired boilers are
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poorly controlled devices with tuning or optimization occurring at monthly or yearly
intervals rather than on a continual basis. Here operating point control could be used to
alter the local fuel/air ratio and provide continuous flame optimization to improve overall
system efficiency.

Future Plans

Measurements are planned to investigate the use of the rapid-response temperature
sensor for closed loop control of a swirl-stabilized laboratory flame. Here we are poised
to investigate the feasibility and potential for active combustion control of instabilities in
an important practical class of combustors, i.e. gas turbine combustors.

Measurements to demonstrate the use of the wavelength-multiplexed sensor to
optimize coal-fired power plants are underway with our industrial partner, Zolo
Technologies. Here there is significant potential to bring modern operating-point control
to the coal-fired production of electricity.

The development of a new class of fuel sensors is only now emerging, however these
sensors may also offer high potential for combustion control.

Publications

1. Xin Zhou, Xiang Liu, Jay B. Jeffries, and Ronald K. Hanson, “Fast Fiber-coupled Diode Laser
Temperature Sensor Using H2O Absorption for Combustion Control,” 43rd Aerospace Sciences
Meeting and Exhibit, AIAA, January, 2005.

2. A. Sappey, J. Howell, P. Masterson, H. Hofvander, J. B. Jeffries, X. Zhou, and R.K. Hanson,
“Determination of O2, CO, H2O Concentrations and Gas Temperature in a Coal-Fired Utility Boiler
using a Wavelength-Multiplexed Tunable Diode Laser Sensor,” Work-in-Progress Poster, 30th

References


5. S.T. Sanders, J.A. Baldwin, T.P. Jenkins, D.S. Baer, and R.K. Hanson, Proceeding of the Combustion

absorption diagnostics for measurements in practical combustion flow fields” 39th

Detection using Multiplexed Diode Lasers for Rapid Temperature Measurements in Gaseous Flows,”

Contacts

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Dr. Jay B. Jeffries: jay.jeffries@Stanford.edu
II.4.4 Characterization of Coal and Biomass Conversion Behaviors in Advanced Energy Systems

Investigators
Reginald E. Mitchell, Associate Professor, Mechanical Engineering; Paul A. Campbell and Liqiang Ma, Graduate Researchers; Lars Sørum, Visiting Scholar

Introduction

The goal of this project is to develop models that predict accurately coal and biomass gasification and combustion behaviors in the type environments likely to be established in advanced energy systems. This requires acquiring the information needed to understand and characterize the fundamental chemical and physical processes that govern coal and biomass conversion at high temperatures and pressures. The models can be used to determine operating conditions that optimize thermal efficiency and to examine design strategies for integrating combined cycles for the production of synthesis gas and electric power with minimum impact on the environment.

There is considerable concern regarding the potential global environmental impact of fossil fuels used for power generation. Carbon dioxide emissions are among the concerns. Coal will play a significant role in meeting the world’s energy demands for the next fifty to one hundred years even if hydrogen becomes the primary energy carrier. By increasing the fraction of renewable energy in the energy supply, the extent to which carbon dioxide emissions will impact atmospheric properties can be mitigated. Biomass is a renewable fuel, and is considered as being CO₂-neutral with respect to the greenhouse gas balance if the use of fossil fuels in harvesting and transporting the biomass is not considered. Co-firing biomass with coal in traditional coal-fired boilers and furnaces or using biomass-derived gas as a reburn fuel in coal-fired systems represent two options for combined renewable and fossil energy utilization. Configurations that employ both biomass and coal in integrated gasification, combined gas and steam power cycles and hybrid technologies that produce synthesis gas for fuel cells as well as produce electric power in combined gas and steam power cycles offer additional options.

Presently, the United States Department of Energy’s Office of Fossil Energy is considering developing hybrid gasifier-combustor energy systems as the core technology for the Department’s Vision 21 energy plant of the future [1]. Hybrid technologies are well suited for combined renewable/fossil energy utilization. A number of potential approaches to the co-utilization of coal and biomass have been the subject of demonstration projects, both in Europe and the United States [2]. The selection of any particular co-firing option is likely to be made on the basis of minimum interference with normal operation of the coal-fired facility with minimum impact on its environmental control equipment. The design of efficient coal/biomass co-utilization energy systems with integrated thermal management to minimize waste heat requires an understanding of the processes that control the physical transformations that fuel particles undergo when exposed to hot environments and the chemical reactions responsible for conversion of the solid material to gaseous species and ash. The goal of this project is to provide the needed understanding. Our efforts will result in fundamentals-based sub-models for particle mass loss, size, apparent density, and specific surface area evolution during
conversion of coal and biomass material to gas-phase species during gasification and combustion processes.

Background

In the high-temperature oxidizing environments established in coal-fired boilers and furnaces, the char particles formed subsequent to coal devolatilization burn with decreases in both size and apparent density, and the relative changes in size and density depend upon the extent of char conversion. To capture this effect, models that accurately characterize overall mass loss rates during gasification and combustion at high temperatures must be based on the intrinsic chemical reactivity of the carbonaceous particle material, and parameters that control the mode of burning must depend on char reactivity. Such models have been developed and partially validated in ongoing work in our laboratory [3-6]. A variety of coals, biomass materials and synthetic chars have been tested to determine parameters that describe char reactivity as a function of temperature and reactive gas concentration. In a related study [7], a model for the mode of char particle burning was validated for coal chars and the chars of biomass materials that are relatively friable (and hence, can be pulverized). Almond shells and wood chips fall into this category. Straws do not.

In our experimental approach, chars characteristic of those created at high temperatures and heating rates in actual coal-fired boilers and furnaces are produced in a laminar flow reactor. By properly adjusting the flow rates of the gases (CH₄, H₂, O₂, and N₂) fed to the diffusion-flamelet burner of the flow reactor, gaseous environments can be established inside the reactor that have a specified oxygen content (from trace amounts to 12-mol-% O₂) at specified temperature (from 1300 to 2000 K). Size-classified samples of the materials to be examined (coals, biomass materials, synthetic chars, and chars to be heat-treated) are fed along the centerline of the flow reactor and partially reacted chars are extracted at selected residence times (up to 200 ms) using a solids sampling probe. The extracted samples are analyzed to determine char physical and chemical properties as functions of char conversion. Particle size distributions are measured using a Coulter Multiziser, an instrument that measures the size distributions of particle suspensions using an electroresistive method. Apparent densities of particles are measured using a tap density procedure in which packed-beds of particles in a graduated cylinder are weighed. Specific surface areas of particles are determined from carbon dioxide adsorption measurements employing CO₂/He mixtures at 298 K and 10 atm. Intrinsic char reactivities to oxygen are determined from oxidation tests performed in a pressurized thermogravimetric analyzer (PTGA) under chemical kinetics-controlled reaction conditions. Analytical procedures are discussed in various publications [3-7]. The data are used to validate and to determine parameters in the sub-models developed.

Chars for testing are also produced in a tube furnace in nitrogen environments at temperatures up to 1000 °C at low heating rates (less than 50 °C/min). These chars are representative of those formed in grate furnaces, where particles experience a wide range of heating rates in volatiles-rich environments. These chars are also subjected to oxidation tests in the PTGA so that their intrinsic reactivities can be determined.

Figure 1 shows results of a typical oxidation test when wood chips are exposed to 10 mol-% O₂ at 500 °C. After the sample has been put in the PTGA balance pan and the
PTGA is closed, the reaction chamber is purged with nitrogen for 53 min at room temperature to ensure an inert environment. Any CO₂, CO or air, remaining in the reaction chamber is eliminated during this time. After 53 min, the temperature is ramped up to the reaction temperature of 500 °C in 20 min, still in an oxygen-free environment in order to dry the sample. As can be observed from the flat portion of the weight profile from 75 to 90 min, the sample is dry before oxygen is admitted. During this heating and drying of the sample in nitrogen, a small amount of CO and CO₂ is released (desorbed). These carbon oxides are formed from oxygen complexes in the initial char sample.

Figure 1: Experimental results from a typical oxidation test in 10 vol-% O₂ at 1 atm.

At 90 min, the reaction gas (10 vol-% O₂ in nitrogen) is turned on. From 90 to 330 min, the sample is kept at a constant temperature (500 °C) and in a uniform and constant gas composition. During the reaction period the oxygen reacts with the carbon in the sample, producing CO and CO₂, which are subsequently released, reducing the mass of the material on the PTGA balance pan. At 330 min the reaction gas is turned off and the sample is once again purged with nitrogen, making sure that the sample is no longer reacting. At 378 min, still in nitrogen, the sample is heated up till 1100 °C in order to remove any adsorbed oxygen complexes remaining on the material in the balance pan. This yields the true sample mass at the end of the test. The oxygen on the sample during this desorption is released as CO and CO₂ if there is still carbon left in the sample.

The mass profile between 90 and 330 min is differentiated to determine the overall conversion rate in the environment established in the PTGA. The char particles are assumed to consist of two components: an ash fraction, which is assumed to be non-reactive, and a carbonaceous fraction, which is assumed to react, forming both CO and
CO₂. The specific mass loss rate of the char \(R_c\) is expressed in terms of the mass loss rate and specific surface area of the carbonaceous portion of the particle material \(S_{gc}\) as:

\[
R_c = -\frac{1}{m_c} \frac{dm_c}{dt} = \frac{1}{1 - x_c} \frac{dx_c}{dt} = R_{ic} S_{gc}, \tag{1}
\]

where \(m_c\) is the mass of carbonaceous material in the char at time \(t\); \(x_c\) is the fractional char conversion, daf; \(S_{gc}\) is the specific surface area of the carbonaceous material; and \(R_{ic}\) is the intrinsic chemical reactivity per unit specific surface area.

The specific surface area model developed by Bhatia and Perlmutter [8] for porous carbons is used to describe the variations in specific surface area of the carbonaceous particle material with conversion under chemically-controlled oxidation conditions:

\[
S_{gc} = S_{gc,0} \left(1 - \psi \ln(1 - x_c)\right). \tag{2}
\]

Here, \(x_c\) is fractional conversion on a dry, ash-free basis (daf) and \(\psi\) is a structural parameter that can be determined from fits to data. Our in situ surface area data obtained with coal, biomass, and synthetic chars confirm the validity of this model for constant apparent density burning, as is the case when rates of chemical reaction control overall mass loss rates.

The specific surface area of an ash-laden char particle having an ash fraction \(X_{ash}\) after reaction for time \(t\) is assumed to obey the relation

\[
S_{gp} = X_{ash} S_{gp,0} + (1 - X_{ash}) S_{gc}. \tag{3}
\]

\(S_{gp}\) is the quantity actually determined from the CO₂-adsorption measurements. The adsorption measurements taken at the beginning of an oxidation test yields \(S_{gp,0}\), the initial specific surface area of the char particle. Gas adsorption measurements taken at the end of an oxidation test, after all the carbonaceous material has been burned away yields \(S_{gas}\), the specific surface area of the ash. Equations (1) - (3) permit the determination of char reactivity as a function of char conversion using the measured data.

Reactivities determined in PTGA environments of specified temperature and oxygen content provide the data needed to gain an understanding of the important reaction pathways governing char oxidation. In our approach, the following heterogeneous reaction mechanism is used to characterize the reactivities:

\[
\begin{align*}
2C_f + O_2 & \rightarrow 2C(O) \quad \text{(R1)} \\
C_f + C(O) + O_2 & \rightarrow CO_2 + C(O) + C_f \quad \text{(R2)} \\
C_f + C(O) + O_2 & \rightarrow CO + C(O) + C(O) \quad \text{(R3)} \\
C(O) & \rightarrow CO + C_f \quad \text{(R4)}
\end{align*}
\]

Here, \(C_f\) represents a free carbon site, one available for oxygen chemisorption, and \(C(O)\) represents a carbon site filled with a chemisorbed \(O\) atom. It is assumed that each carbon atom represents a potential adsorption site and that desorption of a chemisorbed oxygen atom removes the associated carbon atom to uncover an underlying carbon site, which becomes available for oxygen adsorption.
To date, Arrhenius parameters that describe the reaction rate coefficients for the above reactions have been determined for several coal, biomass, and synthetic chars. All of the chars examined were produced at high heating rates in the laminar flow reactor. Using the kinetic parameters determined from analysis of the data obtained in the PTGA oxidation tests, mass loss rates in the flow reactor can be predicted accurately using a char combustion model that takes into account oxygen transport to the outer surfaces of particles as well as oxygen diffusion through the pores of particles as the particles burn.

**Recent Results**

During the past year, we developed the capability to measure O₂, CO, and CO₂ concentrations in the reaction chamber of the PTGA during an oxidation test. The plumbing and instrumentation needed to monitor the gases just above the sample in the balance pan were installed and the software needed to integrate the signals from the gas detectors with the weight measurements was written and compiled to run on the computer that controls the PTGA. Calibration tests were performed as were validation tests with empty balance pans and non-reactive, inert materials. The O₂, CO, and CO₂ profiles shown in Fig. 1 are indicative of our present capability to make simultaneous gas and weight loss measurements during an oxidation test. These measurements permit better characterization of the rates of reactions R2 and R3 in the heterogeneous reaction mechanism. They provide a direct measure of the heterogeneous CO-to-CO₂ product ratio as a function of temperature.

As part of our effort to assess the extent to which the reactivity of a biomass char can be predicted based on its fractional contents of cellulose, hemicellulose and lignin, three cellulosic-based biomass materials were tested to determine the reactivity of their chars to oxygen. The materials selected (wood chips (WC), newspaper (NP), and glossy paper (GP)) had similar chemical compositions on an ash-free basis, but differed in their ash-content. Proximate and ultimate analyses are shown in Table I.

**Table I:** Proximate and ultimate analyses and specific surface areas of biomass materials and their chars.

<table>
<thead>
<tr>
<th></th>
<th>Proximate Analysis</th>
<th>Ultimate Analysis (daf)</th>
<th>Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VM (wt%)</td>
<td>Fix-C (wt%)</td>
<td>Ash (wt%)</td>
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<tr>
<td>Parent</td>
<td>WC</td>
<td>86.3</td>
<td>13.3</td>
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<tr>
<td></td>
<td>NP</td>
<td>85.9</td>
<td>10.7</td>
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<td></td>
<td>GP</td>
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</tr>
<tr>
<td></td>
<td>NP</td>
<td>9.4</td>
<td>79.1</td>
</tr>
<tr>
<td></td>
<td>GP</td>
<td>21.4</td>
<td>16.8</td>
</tr>
</tbody>
</table>

* Obtained by mass balance

Note the relatively high ash content of the glossy paper. It is likely that the clays and other additives used as filling material to obtain a glossy finish contributed to the non-combustible components of the paper. The compositions of the ashes were somewhat similar, SiO₂ and CaO accounting for about 60% of the weight of the ash of each parent
material. About 35% of the weight of the ash of the glossy paper was unidentified, and is believed to be associated with additives used in processing the paper.

Chars were produced by devolatilizing the biomass materials in nitrogen at low heating rates in a tube furnace maintained at 900 °C. The proximate and ultimate analyses of the low-heating-ratechars are also shown in Table I. Note that the chars still contain some volatile matter. The volatile matter content determined for the glossy paper char is unusually high and so is the value reported for its oxygen content. Since the oxygen content is determined by difference, it is likely that the value reported for the oxygen weight fraction of the glossy paper char includes constituents of the additives used in the finishing process. [The standard ultimate analysis procedure assumes that the organic portion of the material examined only contains C, H, O, N, S, and Cl elements.] Also presented in the table are the specific surface areas determined for the char particles. Note that the specific surface areas of the carbonaceous portions of the chars are similar.

Intrinsic chemical reactivities determined for the chars of the three cellulosic-based biomass materials when exposed to 10 mol-% oxygen at 500 °C are presented in Fig. 2. One of the newspaper chars was heat treated by injecting the char produced in the tube furnace into the laminar flow reactor when an environment containing trace levels of oxygen at 1550 K was established. This char is labeled NP-HT; its reactivity is also shown in the figure.

![Figure 2: Intrinsic reactivity ($R_{ic}$) as a function of char conversion ($x_c$).](image)

The results reveal that the reactivities of the cellulosic-based chars selected for study vary with conversion. All the chars have peak reactivity at low conversions ($x_c < 0.03$, daf). At the onset of oxidation, these low-heating-rate-produced chars exhibit a rapid increase in reactivity followed by a rapid decrease. At ash-free conversions greater than about 0.15, char reactivities are factors ranging from 3 to 6 below the peak values, and
II.4 Project Results: Advanced Combustion

remain at these relatively low levels until the final stages of burning. Note that subjecting the newspaper char to a higher temperature had a relatively minor effect on its reactivity. The heat-treated char does not, however, exhibit as sharp a peak as its parent char at the onset of oxidation. It should be noted that all of the coal and biomass chars that we have previously examined were produced at high heating rates and none of the chars exhibited such sharp initial peaks in reactivity as observed with these chars that were produced under low heating rate conditions.

The reactivity profiles of the chars produced at low heating rates are possibly the consequence of the carbonaceous material consisting of two components, one that is more reactive than the other. The initial peak in reactivity is due to the highly reactive portion of the char, which is quickly consumed once the char is exposed to oxygen at high temperatures. It may be that the more reactive portion of the carbonaceous material is associated with the volatile matter content of the char. Low heating rates provide opportunities for primary devolatilization products to undergo secondary reactions and reattach to the carbonaceous matrix as they diffuse through devolatilizing particles. Such reattached fragments are likely to be measured as volatile matter during a proximate analysis. The glossy paper char has the highest peak reactivity; it also has the greatest amount of volatile matter, as indicated by the proximate analysis. The peak reactivities of the wood chip and newspaper chars are comparable; so are the volatile matter contents of their chars. Additional tests are planned to determine if this is indeed the case. In order to predict the types of reactivity profiles exhibited by these low-heating-rate chars, it is necessary to modify our heterogeneous reaction mechanism to include two types of carbon sites, one type being more reactive than the other. Such modifications are being considered.

The data obtained with the glossy paper chars indicate a possible impact of the ash in the char on inhibiting char oxidation rates near burnout. Note that the reactivity profile for the glossy paper char falls to nearly zero at about 58% conversion, daf. The char particles at this extent of conversion are ash-rich, containing more than 75% ash by weight. It is likely that the ash plays a role in limiting the reactivity of the char by, for example, encapsulating the carbonaceous material, rendering it more difficult for oxygen to reach the carbonaceous surfaces where it can be adsorbed. By the time the wood chip and newspaper chars are 75% ash by weight, char conversion is over 95%, daf. Any ash inhibition effects are minor for these low-ash materials. Studies are underway to shed insight into the possible inhibiting effect of ash, an important effect for biomass materials having high ash contents.

Future Plans

Studies to determine the relationship between coal and biomass properties and model parameters are ongoing as are studies to characterize the impact of the ash-content of particles on char reactivity. A particular goal of our current research is to characterize the impact of total pressure on coal- and biomass-char reactivity. To this end, coal and biomass materials are being subjected to oxidation tests at high pressures. Our heterogeneous reaction mechanism will be modified to reflect our latest understanding of rates of the key chemical reactions controlling the conversion of the carbonaceous solid material to gas-phase species. The objective of one of our studies is to assess the extent to which the reactivity of a biomass char can be predicted based on its fractional contents.
of cellulose, hemicellulose, and lignin, the principle building blocks of biomass materials. Towards meeting this goal, cellulose-rich, hemicellulose-rich, and lignin-rich biomass materials are being identified and will be tested to determine the reactivity of their chars to oxygen.

The work being performed will allow us to characterize accurately the chemical and physical changes that coal and biomass particles undergo during combustion and gasification processes. The studies undertaken will help us to understand how coal and biomass properties influence char conversion rates in high-temperature, high-pressure environments. The data obtained will permit the development and validation of the physical and chemical sub-models needed in comprehensive models for coal-fired and biomass-fired process units. The comprehensive models can be used to investigate potential design strategies and can help define optimum operating conditions that yield high coal and biomass conversion efficiencies with minimum impact on the environment.

References


Contact

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II.4.5 Process Informatics Model (PrIMe): A Systematic Approach to Building Combustion Chemistry Models

Investigator
David M. Golden, Consulting Professor, Mechanical Engineering

Introduction
Development of new energy-efficient low-emitting combustion technologies requires models for the combustion process that combine sub-models for combustion chemistry, heat and mass transfer, and fluid mechanics. A major limitation in developing these process models is the availability of accurate, validated, and computational tractable combustion chemistry models. This research is aimed at the development of a new approach for constructing and reducing models of complex chemical reactions. It has been termed Process Informatics. This endeavor is made possible by recent advances in computer science that allow assembly and manipulation of large amounts of data that may be scattered over different sources using Web-based computer networks. The goal is to convert combustion chemistry model building into science, to automate the methodology, and to make the information available in a prompt and convenient form on the Internet for researchers and designers of combustion equipment.

Background
A good deal of the effort in this project is in essence political. That is, it involves community organization in the combustion research community and it requires the acceptance of a somewhat different paradigm than the standard in the community. External developments in the field in the past year involve several workshops and symposia in which the PrIMe idea has been gaining currency. Presentations by the PI, Professor Golden, as well as American collaborators at UC Berkeley, SRI International and international collaborators from the UK and the Continent and other such developments are discussed below in the “Results” section of this report.

In addition, the National Institute of Standards and Technology (NIST) has agreed to be the permanent host for the PrIMe Library and eventually for the computer based tools required for model development. Some of these tools are being developed in a Sandia National laboratory led effort called, Collaboratory for Multi-scale Chemical Science (CMCS). Initially PrIMe will be available at Sandia as well. Professor Golden is a member of the Advisory Board of CMCS. Interest in industry is picking up with the attached endorsement from a major engine manufacturer. (Final company approvals are still pending, so the company name is omitted here.)

Results
The first goal of the PrIMe project is the creation of a database or library, sometimes even referred to as a warehouse for combustion data. The goal is an agreed upon, evaluated by the community, updated in a timely fashion, data library. The library is open, accessible to all and contains, beside the agreed upon values, all data and all
dissents from the consensus evaluation. There are some models for this type of activity, Professor Golden has been a member of the NASA/JPL Panel that evaluates rate data for atmospheric modeling, but the goal here is more far-reaching. All background information used in the evaluations will be available.

This program requires bringing a large community together and it has been somewhat slower than hoped. Professor Golden, Professor Michael Frenklach of the University of California, Berkeley and Professor Michael Pilling of Leeds University have acted as a “troika” in engaging the community. Prominent additions to the active team include Dr. Wing Tsang of NIST, Professor William Green of MIT and Dr. Jeremy Frey of The University of Southampton, UK. Many other workers have expressed their willingness to participate. In addition to the normal human factors, there has been a good deal of effort spent on understanding intellectual property matters.

The first informal gathering of possible PrIMe participants took place during the International symposium on Combustion in Sapporo, Japan in August 2002.

Professor Frenklach made a presentation at the DOE Basic Energy Sciences Contractor’s Meeting in Lake Tahoe, CA in May 2003 that outlined possibilities associated with this project. He and colleagues have published an article1 in December 2003 that points out the large amount of information available from extant experiments that is not being accessed as result of lack of familiarity with many statistical procedures that can now be accomplished with relative ease.

A meeting at NIST in September 2003 aimed at establishing a data base for “Real Fuels” served as a venue for discussions that resulted in NIST becoming the home for PrIMe. At that meeting Professor Golden explained the procedures used to develop the widely used Natural Gas combustion mechanism, known as GRI-Mech. He pointed out all the ways this could be better accomplished once PrIMe is underway. Professor Frenklach, once again described the future of process modeling.

In March 2004 there was a symposium in the Fuel Section of the National American Chemical Society Meeting in Annaheim, CA. Two days of speakers discussed combustion modeling and PrIMe was a central focus in several presentations. (The agenda is attached and those presentations directly involving PrIMe related activities are highlighted.) A presentation based on collaboration with Professor William Lester, Professor Frenklach and students at UC Berkeley, includes Professor Golden and is listed below.

At this time all the background data used in developing the GRI-Mech model has been cast into XML format and the very large amount of data available at Leeds University will be translated and made available for PrIMe.

Dr. Gregory P. Smith of SRI International, Menlo Park, CA has together with Professor Frenklach and colleagues at Berkeley, applied the tools of process informatics
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to understanding a dichotomy in the understanding of OH chemistry in the upper stratosphere and the lower mesosphere. A paper is being prepared.\(^2\)

**Progress**

In the instructions for this report we were asked to provide a discussion of the progress achieved to date toward the goal of developing the basis for technology options that could lead to substantial reductions in emissions of greenhouse gases that result from energy use. In other words, describe the potential impact of the research, if successful, on greenhouse gas emissions at a global scale.

This is a far-reaching goal. The best illustration of the future use of PrIMe for this purpose is found in the engine manufacturer letter of support. The goal is to make modeling and design of combustion driven devices easier and accurate, with the goal of energy efficiency and minimal pollution of all kinds.

**Future Plans**

This research project is really the tip of an iceberg. There will be ongoing work in codification of data in XML format and I putting together the evaluation teams. There will be an ongoing attempt to secure funding for a large scale collaborative effort. Colleagues at NIST are spearheading an effort to secure NSF support. Hopefully the modest support for Professor Golden will allow his continued participation.

**Publications and Presentations**

1. Evaluating and Codifying Data for Engineering Applications
   Presented by David M. Golden at NIST Workshop on Real Fuels, September 2003

   Presented by Alexander C. Kollias at the American Chemical Society National Meeting, March 2004

**References**

1. Collaborative data processing in developing predictive models of complex reaction systems

   Gregory P. Smith, Michael Frenklach, Ryan Feeley, Andrew Packard, and Peter Seiler

**Contact**

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**Attachments**

I: Engine Manufacturing Company Support for PrIMe
II: NIST Announcement of PrIMe Involvement
III: Agenda from Fuel Chemistry Symposium at ACS National Meeting March 2004
Attachment I: Engine Manufacturing Company Support for PrIMe

To whom it may concern: (This should be changed to the specific individuals that we need to target. We have not determined who they are yet.)

There is a proposed project, called PrIMe, with NIST and a few other individuals from universities and national laboratories that will be of utmost importance to us at this company. The importance is due to our efforts to meet the 2010 emission regulations. This is a very short time frame for technology that is highly new and innovative. It has to be highly innovative and new because of the super low levels of regulation required. In recent years, the levels for exhaust emissions required by law have been dropping at a rapid rate. This is going to require some extreme changes, and we need your help.

This company, like all manufacturers of heavy-duty engines, makes extensive use of computer simulations; but we need much more than just new and more capable computers. There are fundamental areas of science in which we are desperate for better definition. One of the areas is the chemical process that controls the generation of the emission species. We need a much better definition of the reaction paths from diesel fuel to products of combustion, including nitrogen oxides and particulates (soot). We recently attended a meeting at NIST where we discussed this problem, and were concerned with the lack of support received by scientists working in this area. However, we were able to put together a program that we feel is excellent and will go a long way to help us in this endeavor. Now we must ensure that this program receives the funding and support that it needs. We wish we had this 15 years ago, but we did not.

The fact that NIST has joined PrIMe is one of the essential steps necessary to insure that we obtain accurate models, so we endorse this action by NIST.

We understand that our competitors overseas are ahead of us in the US in these areas. We do not mind competing with them on an equal basis, but it is unnerving to compete while our science is behind.

The people that we consider to be essential to this project include:

Michael Frenklach, U. C. Berkley and Lawrence Berkeley Laboratory
David Golden, Stanford U.
Wing Tsang, NIST

There may be others, but the people listed above are best at answering whom they should be. We are prepared to cooperate with them in anyway we can.

Thank you for your consideration,
II.4 Project Results: Advanced Combustion

Attachment II: NIST Announcement of PrIMe Involvement

NIST joins the PrIMe Initiative within the combustion research community

The PrIMe initiative is a community effort to generate data libraries, analysis software, and the supporting information technology infrastructure that will enable a collaborative approach to development of predictive models of combustion. NIST has recently joined the PrIMe initiative. In its initial focus NIST will seek to enable achievement of PrIMe’s first objective, i.e. the creation of the PrIMe Data Warehouse. This warehouse is visualized as a comprehensive repository of all data relevant to modeling combustion processes. Development of this library is a community project involving submission and evaluation of the data, often presented in the form of a “mechanism”, describing various combustion scenarios. Evaluation at this stage is concerned with the data required for quantitatively describing the chemical reactions within the mechanism and a measure of the uncertainty of the data. In addition, the evaluation will seek to discern a clear documentation as to the sources of the data and associated uncertainties; this documentation is often termed the traceability or pedigree of the data.

NIST’s commitment to the PrIMe initiative envisions creating new paradigms for scientific collaboration. This new paradigm relies on an information technology infrastructure which is currently under development in the Collaboratory for Multiscale Chemical Science (CMCS) and our efforts will rely on CMCS infrastructure and use their facilities. As a first step, the NIST Gas Phase Chemical Kinetics Database and the GRI-Mech 3.0 dataset, a consensus mechanism for combustion of C1 and C2 hydrocarbons, will be incorporated into the PrIMe/NIST Data Warehouse. Harmonization of data schema and XML data exchange standards and development of selected IT tools will be required in this first step. A data submission and a data query interface also will be developed to facilitate population of the Warehouse and open access to these data by the research community. Although the PrIMe/NIST Data Warehouse currently is focused on the combustion of hydrocarbon fuels, the Warehouse could logically extend to include other areas such as atmospheric chemistry. The new collaborative paradigm envisioned for combustion research may well benefit other research areas and increased information exchange amongst many diverse communities should benefit all.

It is planned to have an alpha version of the PrIMe/NIST Data Warehouse operational by the end of March 2004.
### Attachment III:

**Agenda from Fuel Chemistry Symposium at ACS National Meeting March 2004**

**Molecular Modeling and Reaction Chemistry**

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<tr>
<th>Time</th>
<th>Title</th>
<th>Authors</th>
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<tbody>
<tr>
<td>8:00 AM</td>
<td>Introductory Remarks</td>
<td>Hai Wang</td>
</tr>
<tr>
<td>8:10 AM</td>
<td>Detailed chemical kinetic modeling: Is there life after GRI-Mech 3.0?</td>
<td>Henry J. Curran</td>
</tr>
<tr>
<td>9:00 AM</td>
<td>Efficient lumping technique for the automatic generation of n-heptane and iso-octane oxidation mechanism</td>
<td>Syed Sayeed Ahmed, Gladys Moréc, Thomas Zeuch, Fabian Mauss</td>
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<tr>
<td>9:25 AM</td>
<td>Automatic optimization of detailed kinetic mechanism for HCCI-engine simulation</td>
<td>Raffaella Bellanca, Fabian Mauss, Hai Wang</td>
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<td>9:50 AM</td>
<td>Development and use of rate-constrained chemical equilibrium with HCCI combustion modeling</td>
<td>Scott B. Fiveland, Chris Rutland WITHDRAWN</td>
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<tr>
<td>10:15 AM</td>
<td>Intermission</td>
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<tr>
<td>10:25 AM</td>
<td>Surface reactivity as a many body multiscale problem</td>
<td>Ashish B Mhadeshwar, Jeff Ludwig, Abhijit Chatterjee, Dionisios G Vlachos</td>
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<tr>
<td>11:05 AM</td>
<td>Importance of gas phase kinetics within the anode channel of a solid oxide fuel cell</td>
<td>Chad Sheng, Anthony M. Dean</td>
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<tr>
<td>11:45 AM</td>
<td>Computational studies of boron/nitrogen and aluminum/nitrogen compounds for chemical hydrogen storage</td>
<td>Maciej Gutowski, Tom Autrey</td>
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<td>1:30 PM</td>
<td>Developing and using mechanisms for the oxidation of organic compounds in the atmosphere</td>
<td>Michael Frenklach, Ryan Feeley, Andrew Packard, Pete Seiler</td>
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<tr>
<td>2:20 PM</td>
<td>Ab initio study of the oxidation of NCN by O₂</td>
<td>R. S. Zhu, M. C. Lin</td>
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<tr>
<td>2:45 PM</td>
<td>The molecular origins of NO selectivity in the thermal reduction of NOₓ by NH₃</td>
<td>Donghai Sun, W. F. Schneider, J. B. Adams, D Sengupta</td>
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<tr>
<td>3:05 PM</td>
<td>Intermission</td>
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<tr>
<td>3:20 PM</td>
<td>Computer aided design of complex chemical mechanisms for combustion applications</td>
<td>Fabian Mauss</td>
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<td>4:10 PM</td>
<td>New methods for predictive chemical kinetics</td>
<td>William H Green Jr., Binita Bhattacharjee, Oluwayemisi Oluwole, Jing Song, R. Sumathi, Catherina D Wijaya, Hsi-Wu Wong, Paul E. Yelvington, Joanna Yu</td>
</tr>
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<td>4:35 PM</td>
<td>Pressure-dependent automated mechanism generation: Systematic models for difficult systems</td>
<td>David M. Matheu, Anthony M. Dean, Jeffrey M. Grenda</td>
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<tr>
<td>5:00 PM</td>
<td>Simulation of light petroleum fractions</td>
<td>Tareq A. Albahri</td>
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<td>8:00 AM</td>
<td>Optimization and consistency of a reaction dataset</td>
<td>Michael Frenklach, Ryan Feeley, Andrew Packard, Pete Seiler</td>
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<td>169</td>
<td>Reactivity extrapolation from small to large molecular systems via isodesmic reactions for transition states (RESLIR) Vadim D. Knyazev</td>
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<tr>
<td>9:05 AM</td>
<td>170</td>
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<td></td>
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<tr>
<td>9:40 AM</td>
<td>171</td>
<td>The high temperature decomposition of hexyl radicals</td>
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<td>172</td>
<td>Multi-channel chemically activated reactions: Comparison of Troe’s weak collision model and solution of collisional energy transfer by Monte Carlo method Ameya V. Joshi, Scott G. Davis, Hai Wang</td>
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<td>173</td>
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<td>175</td>
<td>Thermodynamics of Jahn-Teller molecules Timothy A. Barckholtz</td>
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<td>1:00 PM</td>
<td>192</td>
<td>Reaction paths, kinetics and thermochemical properties in the dimethylsulfide radical reaction with O2: CH3SC·H2 + O2 Joseph W. Bozzelli, Fei Jin</td>
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<td>194</td>
<td>Thermochemical and kinetic analysis of the allyl radical with O2 reaction system Joseph W. Bozzelli, Jongwoo Lee</td>
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<td>Computational study of the oxygen initiated decomposition of 2-oxepinoxy radical John K. Merle, Christopher M. Hadad</td>
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<td>Hydrogen atom catalyzed isomerization of aromatic compounds Mark Nimlos, Jonathan Filley, J. Thomas Mckinnon</td>
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<td>3:15 PM</td>
<td>197</td>
<td>Combination and disproportionation reactions of alkyl radicals: An ab initio kinetics study for CH₃ + C₂H₅R. S. Zhu, Z. F. Xu, M. C. Lin</td>
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<td>3:40 PM</td>
<td>198</td>
<td>Ab initio quantum chemical studies of hydrogen abstraction reactions of hydrocarbons David W. Ewing, Michael J. Manka</td>
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<tr>
<td>4:05 PM</td>
<td>199</td>
<td>Methyl radical and shift reactions with aliphatic and aromatic hydrocarbons: Thermochemical properties, reaction paths, and kinetic parameters Leonhard K. Rutz, Henning Bockhorn, Joseph W. Bozzelli</td>
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<td>200</td>
<td>Theoretical study on the mechanism of Ni(d10 1S)+CO2+3H2→NiO+CH4+H2O reaction Changwei Hu, Song Qin, Anmin Tian</td>
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III. Analysis Activities

III.1 Introduction to Analysis Activities

Analysis activities are conducted at GCEP to support the construction and redistribution of its technical portfolio and monitor the impact of its research. This Chapter reports progress in technical analysis activities that are performed for the overall project. The first is a Systems Analysis project, led by A. J. Simon of the GCEP staff. This effort is intended to provide a capability for tracing of mass and energy flows for energy systems, so that quantitative comparisons of energy technologies can be made, and to make that capability available for general use via web-based tools. The second is a project entitled Integrated Assessment of Energy Technologies, led by Professors John Weyant and James Sweeney in the Management Science and Engineering Department. The Integrated Assessment project is aimed at developing a comprehensive analysis system that can be used to estimate probable significance of technologies, to explore options to speed up diffusion of technologies, and to determine the magnitude of potential reductions in greenhouse gas emissions.

Figure 1: Analysis Activities
These analysis activities are related through the larger structure of GCEP as illustrated in Figure 1. The primary purpose of GCEP is, of course, to produce new energy technologies with positive economic and climatic impact. The GCEP technical projects, at the bottom center of the figure, represent this activity. The technology assessments, in the center of the figure, serve as the main vehicle through which GCEP makes its decisions to investigate specific technologies. The assessments are performed in concert with systems analysis and integrated assessment. Integrated assessment, in the upper right-hand corner, provides a measure of the potential impact of technology development in the context of infrastructure cost and with respect to the probabilities of success for other technologies. Systems analysis, on the left side of the figure, provides a theoretical bound on performance predictions for new technologies and a set of tools to analyze the performance of developed technologies. Furthermore, detailed systems analysis efforts can be used to advise the integrated assessment effort on the scale of equipment needed to accomplish a certain energy conversion task. The result of these interactions is a detailed technical understanding of a proposed project, a thorough survey of the state-of-the-art and a reasonable estimate of the potential impact. While each of those components could stand on its own merit, the integrated combination will provide GCEP with a high level of confidence in its technology portfolio.
III. Analysis Activities

III.2 Energy Systems Analysis

Investigators
A.J. Simon, GCEP Energy Systems Analyst; Daniel Braithwaite, Jennifer Brantley, Wes Hermann, Rishabh Kasliwal, Brooks Moses, Katie Plzak, Graduate Researchers

Introduction
The Energy Systems Analysis group is a part of the GCEP central assessment effort. The group's main focus is on building quantitative models of mass and energy flow through existing and proposed energy technologies. The technologies under study encompass the same range of subjects that GCEP is investigating: harvesting, storage, distribution, conversion and use of energy. The models under construction are highly detailed and technical in nature. Each model tracks the inputs and outputs as well as all known intermediate states for the material and energy streams used by a device. Such models can pinpoint the most efficient and least efficient steps of device operation, and provide the researcher with a quantitative understanding of the technological challenges associated with a particular device or technology.

These models serve as tools, which aid GCEP in identifying areas where technological innovation can increase the efficiency or reduce the emissions of energy conversion devices and systems. The tools may also predict synergies between multiple technologies as the models are compiled into an integrated framework. The actions of the group serve to train the next generation of energy system engineers (graduate researchers) to think critically about energy and material "round-trip" effects.

The basis of the models is exergy analysis, whereby the irreversible steps in energy conversion processes are identified, quantified and compared to reversible, or ideal, models of energy conversion. The Energy Systems Analysis Group is taking a bottom-up approach to energy system modeling, composed of three phases:

1. Device-Level Modeling
2. Fuel Chain Analysis
3. Energy Network Scenario

Device-Level Modeling
As a first step, individual devices are identified with their associated inputs and outputs. The relationships between the properties of mass and energy as they enter and exit the system are determined by the system model. Model parameters are linked to known state transitions within the system and to material and kinetic constraints. Each model is a self-contained module which can be independently run and verified, and is fully documented with respect to usage, governing equations and reference material. Models can be simple, time invariant, zero-dimensional models as shown for a Molten Carbonate Fuel Cell (MCFC) in Figure 1. However, more detail may be needed, in which case more complex 1-dimensional or quasi 2-dimensional models that track gradients and their associated effects on efficiency will be built. Figure 2 shows a schematic of such a model, used to simulate the MCFC stack.
III. Analysis Activities

Fuel-Chain Analysis

Subsequently, these individual modules will be put together for fuel-chain-analysis. This first level of integration may be as simple as a gas-turbine model connected to a flue-gas-CO₂-separation model. However, it is anticipated that significantly more complex models will be built, such as a Coal to Hydrogen to Fueling Station to Cryogenic Storage to PEM to Electric Motor model. Such a model would serve to identify mass and energy conversion steps with significant inefficiencies or irreversibilities. A part of such a model, with options for liquid or compressed H₂ and two CO₂ shipment options is shown in Figure 3. These models will be built on a "well-to-waste" philosophy, which tracks the resources needed to run all of the internal components, and follows the energy and mass until it is returned to a state in equilibrium with the environment. A sequential chain of devices can be used to account for inefficiency, while a branched model can be used to compare various fuel chains.

Energy Network Scenario

Eventually, energy network models will be built from individual components, chains, and distribution scenarios. It is important to note that the component models will not lose any fidelity during this scale-up process. In this way, the effects of real technology development on energy infrastructure can be estimated.

Figure 1: 0-D Fuel Cell Model

Figure 2: Quasi 2-D Fuel Cell Model

Figure 3: Fuel Chain Analysis Schematic
III. Analysis Activities

Background

Large reductions in CO₂ emissions will undoubtedly be accompanied by vast changes in infrastructure. The anticipation of such changes has touched off significant activity in the realm of "Systems Analysis." There are two main reasons for this activity:

First, significant innovation is required to move towards a low greenhouse gas (GHG) energy system. This innovation is likely to come from individuals or groups who have a deep understanding of energy issues. Systems Analysis is an effective method of developing such an understanding. Furthermore, candidate solutions to our energy challenges are likely to emerge at the borders of what are traditionally separate systems in the energy world. It is the opinion of this author that waste and inefficiency often occur at boundaries. This phenomenon is certainly true of mechanical systems (composed of mass and energy) where exergy destruction drives transport across component boundaries. However, losses at boundaries occur in economic and political systems as well, where waste, or welfare loss, can be attributed to imperfect communication. Integrated Systems Analysis efforts can pinpoint inefficiencies at boundaries and suggest areas where innovation can improve operation.

Second, in the context of GHG emissions, the energy industry is understandably concerned about adopting large-scale changes in technology. The industry has evolved according to economic principles, and has so far been successful in providing for its customers while remaining profitable. However, a lack of understanding of the consequences (and indeed, the absence of an incentive to discover any unintended consequences) of large scale energy use has placed the industry in a tenuous position. As such, all of the parties concerned with a transition to a low GHG energy system want to fully understand the ramifications of that transition. While the stakeholders would like to resolve the GHG issue, no one wants to trade the challenges we are facing now for another set of unidentified challenges. Systems Analysis will help to identify challenges inherent in technologies and policies proposed for a low GHG energy future.

Although Systems Analysis has been recognized as important for the aforementioned reasons, it is still a vaguely defined topic. In the context of energy, the term "Systems Analysis" encompasses (at a bare minimum) modeling efforts aimed at:

1. quantifying the performance of individual devices.
2. characterizing the interactions between various devices.
3. tracking the fate of resources as they are processed through the energy economy.
4. determining the economic feasibility of various energy use scenarios.
5. predicting the economic outcomes of energy policies.
6. finding the causes of, and solutions to, technological, market or policy failure.

While all of those goals are important to the future direction of the energy industry, the GCEP Energy Systems Analysis Group has chosen to focus on the first two. The Systems Analysis Group and Integrated Assessment team (led by Professors Sweeney and Weyant), will work together on the third. The Integrated Assessment effort focuses
on the fourth goal. There are other efforts at Stanford, outside of GCEP, which are
directed at the final two goals.

Analysis of energy systems is taking place at numerous organizations across the

globe; public and private; governmental, corporate and academic. While the projects are
far too numerous and diverse to list here, there are a few efforts that are relatively similar
to GCEP's Energy Systems Analysis.

For example, the International Institute for Applied Systems Analysis maintains a
computer program called CO2DB (Carbon Dioxide DataBase) [1], which is able to
calculate the total GHG emissions from various fuel-chains. The database has a vast
number of entries, but not all are functional, and the model is based on "emissions
factors" rather than physical device models.

A similar database is being constructed by Commissariat a l'Energie Atomique
(CEA), Institut Francais du Petrole (IFP) and Ludwig-Bölkow-Systemtechnik (LBST). This E3 Database [2] is designed to produce analyses for Energy Use, Economics and
Emissions from various energy technologies. The E3 Database has not yet been released
to the public.

Pacific Northwest National Laboratory (PNNL) and the University of Maryland have
established the Global Energy Technology Strategy Program [3], which seeks to model
the energy economy from a technology perspective.

The Center for the Management of Environmental Resources (CMER) at the French
INSEAD campus is studying the trends of large-scale exergy destruction over time [4, 5]. It is hoped that this study will lead to a better understanding of end-use energy efficiency
potential in the future.

The US National Laboratories have several people working on Systems Analysis. Maggie Mann at NREL is leading a team to analyze various energy technologies
associated with hydrogen. Andy Lutz at SNL (California) has worked on a "high-level"
model for predicting GHG emissions from various hydrogen usage pathways. He has
presented some of his preliminary work to the GCEP Systems Analysis Group, and
maintains a dialog with us. Gene Berry at LLNL is working with the energy economists
there on hydrogen technologies and has also presented to GCEP.

**Results**

The Energy Systems Analysis group was established within GCEP in the summer of
2003. Since that time, the group has made significant progress towards its goal of
becoming an integral part of the GCEP assessment process. There are two areas where
the group has met its initial targets: identification of software tools capable of handling
large-scale system-model integration and building component models of energy
conversion technologies.
III. Analysis Activities

**Software**

Several computational tools for the analysis of energy systems have been evaluated and tested for applicability to the Systems Analysis Effort. There are several criteria which the software must meet. It must be easy to program and prototype new models. It should have some thermochemical data embedded. It must be easy to understand how technology sub-components are modeled because new technologies will require modification of simulation parameters. It should be available to the technical community at a reasonable cost so that analysts outside of Stanford can share the models.

Because this is research, there is no commercially available software that satisfies all of the group's needs. Certain tools are undergoing significant in-house enhancements to their functionality. The packages which have been tested are listed here:

- Matlab (from The Mathworks) has been chosen as the programming language of choice for the Systems Analysis Group. Matlab is an extremely flexible programming environment with a wide array of computational tools readily available for adaptation to energy system simulation.
- Cantera (Open Source) is a chemical kinetics package that is being developed at Caltech and in the open source community [6]. The Group is using Cantera for chemical equilibrium calculations and kinetics information, while helping to contribute to Cantera's development through feedback to its primary author.
- Aspen Plus (from AspenTech) was considered as a development environment due to its highly refined graphical user interface and its vast database of thermodynamic properties. However, the Group eventually decided that the modules in Aspen Plus did not reveal enough of their "inner workings" to develop the fundamental understanding of energy systems that is required.
- Aspen Properties (from AspenTech) is a component of the Aspen Engineering Suite which is comprised of databanks of thermodynamic properties for a vast number of substances. Using an ActiveX interface, it is possible to extract data from Aspen Properties in the Matlab work environment. Development of this interface is currently in progress.
- Multiflash (from InfoChem) is another property data package with a Matlab interface available for immediate purchase. Multiflash is being evaluated as an alternative to Aspen Properties.

**Simulations**

The Group has produced several internal working documents, each with an associated software module, on various energy-related subjects and technologies. These modules represent the first batch of results ever produced by the GCEP Systems Analysis Group, and are not yet integrated into fuel chains or scenario models. The task of model integration will take place over the next few years, as more modules are developed (see the Future Plans section below). However, these initial modules lay the groundwork for a much larger model "fleet" which will serve GCEP's ultimate goal of technology assessment.
Four modules are described here, and together they cover a significant fraction of a
potential fuel-chain. The first module is a resource analysis code which returns
theoretical values for the exergy content of a very wide range of energy resources. The
second module is of a waste-to-fuel-gas converter, and the third model is of a Molten
Carbonate Fuel Cell (MCFC). The final module examines a novel CO\textsubscript{2} separation
process. While each of these modules currently stands on its own and is fairly specific in
device performance prediction, the range of models spans resource harvesting, fuel
processing, electricity generation and product-gas treatment.

Summaries of these studies and their key findings are listed below.

Resource Analysis

Exergy is introduced as a tool to assess and compare reservoirs of theoretically
extractable work. These reservoirs contain bulk kinetic energy, potential energy due to a
restoring field, or chemical potential relative to a reference state. This reference state is
derived from the thermal, mechanical and chemical properties of the natural environment.
The paper identifies primary exergy reservoirs and their derivative secondary reservoirs
we call resources. Different exergy formulas are developed depending on the
predominant form of useful energy stored in the material. Resources currently in use or
within the realm of our technology are examined for their quality and quantity. The
results are useful for scrutinizing current utilization and comparing various energy
options independent of technology and cost.

<table>
<thead>
<tr>
<th>Primary</th>
<th>Secondary (Resources)</th>
<th>Replenishment Time Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Celestial Bodies</td>
<td>Tidal</td>
<td>hours</td>
</tr>
<tr>
<td>Solar Nuclear</td>
<td>Solar Radiation</td>
<td>millisecond</td>
</tr>
<tr>
<td></td>
<td>Wind</td>
<td>hours</td>
</tr>
<tr>
<td></td>
<td>Wave</td>
<td>hours</td>
</tr>
<tr>
<td></td>
<td>OTEC</td>
<td>days</td>
</tr>
<tr>
<td></td>
<td>Precipitation</td>
<td>days</td>
</tr>
<tr>
<td></td>
<td>Biomass</td>
<td>years</td>
</tr>
<tr>
<td></td>
<td>Fossil Fuels</td>
<td>millions yrs.</td>
</tr>
<tr>
<td>Terrestrial Nuclear</td>
<td>Geothermal</td>
<td>days - none</td>
</tr>
<tr>
<td></td>
<td>Fission/Fusion</td>
<td>none</td>
</tr>
</tbody>
</table>

Table I lists the various resources available for harvesting and eventual use. It is clear
that solar energy drives almost all of the processes we consider useful for the harvesting
of energy. The only comparable resource would be fusible atomic species already
present on Earth. The paper does NOT quantify the exergy loss in the transformation
from solar energy to the various secondary resources, but it does quantify the exergy
content of the secondary resources with respect to the environment.

The software package associated with this paper calculates the exergy content of unit
quantities of the various resources from literature data and user input regarding the state
III. Analysis Activities

of the resource. For example, the inorganic/hydrocarbon mixture of Tar Sands found in the U.S. has an exergy content of ~6 MJ/kg [7]. This is the absolute upper limit of recoverable work from this resource, and any energy spent harvesting the sands or refining the hydrocarbons will reduce the value.

Armed with estimates of the state and size of each resource, the paper goes on to calculate the exergy content of non-renewable resources and the exergy destruction rate of renewable resources. While the numbers are interesting from a fundamental standpoint, there are enough uncertainties about recoverability factors and environmental consequences of large-scale harvesting that they are not reported here.

Waste-to-Fuel-Gas

A quasi-one dimensional model of a biogasification system has been created based on the anaerobic digestion process. The model analyzes the energy flows and performance of a continuous flow stirred tank bioreactor (CSTR) and a plug-flow bioreactor (PFR) on a thermo-chemical level and predicts the extent of reactions, products formed and other thermodynamic property data. It also measures the inherent performance of the anaerobic digestion process on an energy cum exergy basis. The model is developed for an isothermal reactor (at 25°C) and is flexible with regard to most organic feedstocks. The paper is accompanied by the model code developed in MATLAB and some sample results.

While the Methanogenic Efficiencies (total yield per mole of feedstock consumed) are the same between the CSTR and PFR, the Methane Yield from a PFR is significantly higher. Figures 4 and 5 show that a PFR based methane recovery plant will operate considerably faster or with a considerably smaller footprint than a CSTR based plant.

For a mixture of municipal wastewater and fatty acids, methanogenic organisms are able to convert exergy stored in the substrate to methane with an efficiency of about 55%. This efficiency occurs at a solids-retention-time of approximately 30 days, which implies that the volume of the reactor must be 30 times its daily flow-rate to accomplish complete processing of the waste.
**Molten Carbonate Fuel Cell**

Molten Carbonate Fuel Cells (MCFCs) have many positive characteristics that distinguish them from other energy systems as well as other fuel cells. These features include high temperature operation, carbon dioxide in the oxidant stream, internal reformation, variety of fuel use, potential application to CO₂ separation processes and hybrid system and cogeneration applications. Background information on MCFCs is provided along with a general description of a zero-dimensional representation of the mass and energy flows through a MCFC. Ultimately, an empirically-based, one dimensional molten carbonate fuel cell model is developed.

![Flow Chart of 1-D MCFC Model](image)

**Figure 6: Flow Chart of 1-D MCFC Model**

Figure 6 depicts the iterative scheme used to determine the distribution of current density along the length of the gas flow channel. For an overall cell voltage of 0.74 (assumed as an operating in the leftmost block), it is seen that current density varies from ~2800 to ~2000 A/m² along a channel with a length of 1 m. The activation, ohmic and concentration overpotentials are calculated for each section of the once the current density at that section is known.

The one-dimensional model is useful for quantifying the performance of the cell in terms of first- and second-law thermodynamic efficiencies, for determining fuel and oxidant utilization, and for examining current-density variation along the length of the gas-flow channel. Current density is a major factor in the local efficiency of the cell, as well as "wear" effects such as carbon deposition and local hot-spots.
III. Analysis Activities

**CO₂ Separation**

Reduction of greenhouse emissions from the use of coal for power is essential to a stable, low GHG future. Current methods of carbon dioxide removal from coal fired power plant exhaust and gasification syngas are summarized, and a new method of carbon dioxide removal from pre-combustion gasification syngas is proposed. A model of hydrate formation is used to determine if this method of separation is chemically feasible in an ideal case.

In the proposed system, CO₂ would be trapped in a solid hydrate form, which can be separated from liquid or gaseous components that do not form hydrates. In principle this technique could be used in many stack-gas situations, but would find immediate application in coal-to-hydrogen plants, where CO₂ and H₂ compose the bulk of the flue-gas.

While there is a stable and predictable region of CO₂ hydrate formation at feasible temperatures and pressures (See Figure 7), it remains to be determined whether or not this method of gas separation can be accomplished more efficiently than more established separation processes (PSA, membrane). Furthermore, the three-phase (H₂ gas, liquid water and CO₂ hydrate) nature of the problem will pose significant challenges in reactor design, and the rate of separation may be limited by mass and heat transport considerations.

**Future Plans**

Beyond the four modules described above, several more analyses are in progress, including a survey of emerging water electrolysis techniques and a model of a nuclear fission reactor.

The Energy Systems Analysis effort is planned to continue throughout the existence of GCEP. The main focus of the technical effort will be to implement a broad suite of software modules which analyze the performance of energy systems, and to develop a
framework in which these models can be coupled. The coupling will first take the form
of fuel-chain analyses, and may evolve from there to encompass energy scenarios.

This scenario modeling cannot take place in the absence of economic data. The
Systems Analysis Group will work with the Integrated Assessment Team to build these
detailed scenarios. There is already ongoing dialog between the Systems Analyst and
John Weyant and Jim Sweeney.

As the energy modeling tools become more refined and efficient, they will find use in
the GCEP assessment process. Collaboration between the Systems Analysis Group and
the Assessment Analysts will result in more quantitative assessments as well as more
refined analysis tools. These tools will find applicability to the broader energy
community as they are made public, through internal and external publications and
through an interactive web site.

References
1. International Institute for Applied Systems Analysis:
   http://www.iiasa.ac.at/Research/ECS/docs/data_index.html?sb=18
2. J.M. Agator "Decision Aiding Tool E3 Database for Energetic, Emissions-Related and Economic
   Grenoble, France. 3 Sept. 2003.
3. Pacific Northwest National Laboratory:
   http://www.pnl.gov/gtsp/index.stm
4. R.U. Ayres, B. Warr, "Accounting for growth: the role of physical work." Structural Change and
   Economic Dynamics Accepted for Publication in 2004
6. Cantera, hosted by the California Institute of Technology:
   www.cantera.org

Contact
A.J. Simon: ajsimon@stanford.edu
III.3 Integrated Assessment of Energy Technologies

Investigators
James Sweeney, Professor of Management Science and Engineering; John Weyant, Professor of Management Science and Engineering; Amy Guy, Graduate Researcher.

Background
The research involved two related areas of examination. The first, “Assessing the Value of New Energy Technologies”, focused on two main tasks:

- Developing ways to represent the performance and costs of new energy technologies at representative years in the future probabilistically with and without GCEP support.

- Develop a prototype portfolio valuation model designed to give a probabilistic representation of the contribution of resources invested in each GCEP program area to the overall value of the GCEP portfolio.

The second, “Modeling the Transition to a Hydrogen Economy”, focused on two main tasks:

- Developing a set of unit costs and unit carbon dioxide emissions associated with various technologies that could be used to supply hydrogen for use in light duty vehicles.

- Modeling several quantitative scenarios of the introduction and growth of hydrogen use in light duty vehicles, examining the consequences for economic and environmental impacts as well as impact on other U.S. natural resource use.

These two related areas will be examined separately in the next two sections of this report, entitled “Results: Assessing the Value of New Energy Technologies” and “Results: Modeling the Transition to a Hydrogen Economy”.

Results: Assessing the Value of New Energy Technologies

Advanced Technology Representation
This task has involved alternative ways of representing the performance and cost of fundamentally new energy technologies with and without GCEP funding. So far this has involved assessments of the probability of demonstrating the technical feasibility of the technology and separate assessments of the probability distributions over the cost of employing these technologies to reduce carbon emissions at future dates of interest. We have experimented with triangular, uniform and lognormal distributions.
Also important in projecting the costs of new energy technologies are projected shifts in the assessed distributions over time and decreases in costs with level of implementation resulting from limits on the rate of introduction diffusion considerations, as well as siting, intermittency of availability, and resource supply considerations. Land use, water use, and noble metal availability are examples of resources whose prices may increase if demand for them increases significantly to support the introduction of new energy technologies.

Obviously these assessments require a great deal of input from technical experts in the areas being assessed. So far we have been using our own somewhat limited expertise in the technology areas together with our strong traditional expertise in probabilistic risk assessment and system economics, but we are starting to interact with GCEP’s central systems group and technology assessment staff to bring in their expertise. We hope to involve experts in specific technologies and relevant areas of scientific research here at Stanford and the research community at large in this endeavor. Particularly valuable here will be input from technical experts at the sponsoring companies.

**Portfolio Valuation**

Given information regarding the characteristics of the new energy technologies resulting from R&D (expressed via probability distributions over costs and performance at specific future dates of interest), assessments of the value of that new technology depend on what other new technologies have been developed, the rate of improvement in existing technologies, and conditions in energy markets. Conditions in energy markets are reflected in energy prices and depend on many factors including population levels, economic output, the structures of the world’s economies, resource availabilities, energy producer (and especially oil exporter) behavior, the set of available technologies for producing, transforming and consuming energy, and government energy, economic, and environmental policies.

The key factors that determine the future value of new energy technologies are highly uncertain and the relationships between them can be quite complex. One approach to energy policy assessment is to run sensitivity analysis on external factors through models of the energy system. Figure 1 and Figure 2 show the primary energy mix for 2100 projected by a number of prominent large-scale energy models for a reference case (a different modeler chosen reference case for each model) and a case in which the atmospheric concentration of CO₂ concentration in the atmosphere is limited to 550 ppm.

The changes between the two diagrams are motivated by a tax on carbon that starts at about $10 per ton in the early part of the century and reaches $200 to $400 per ton by 2100 (depending on the model and its reference scenario). Results like these are extremely illuminating, but consider only one reference scenario for one set of parameter values for each model. There are extremely large uncertainties about both over the course of a century and these uncertainties can have a significant impact on how we value the products of long-term R&D on new energy technologies.
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Last year preliminary design criteria for the evaluation framework were developed.

Figure 1. Reference Case World Primary Energy in 2100

Figure 2. World Primary Energy in 500 ppm case in 2100

Design Criteria for Evaluation Framework

Last year preliminary design criteria for the evaluation framework were developed.
It was recognized that large-scale energy system models are often designed for purposes other than long-run energy technology assessment and, therefore, include enough complexities so as to make extensive sensitivity analyses, let alone formal uncertainty analyses infeasible. The approach here is to use reduced form energy models (calibrated to the more large-scale models) as the central element of an uncertainty-oriented technology evaluation approach. We expect to use literature reviews and expert assessments to develop probabilities distributions about key inputs to the models. This is crucial because these inputs are generally more important determinants of the values of the new technologies than the parameters included in the models.

Our experience with thousands of energy system scenarios and hundreds of models over the years enabled us to identify the important drivers of the valuation equations and calibrate them to available modeling results. In addition, we know what information to seek via expert assessments, e.g., ranges of possible economic growth rate assumptions, fossil fuel resource base estimates, evolution of conventional energy technologies, oil exporter behaviors, etc. It will take some time to develop the full assessment system. In the interim, rather than working with all the uncertainties independently, we are working with a set of integrated probabilistic scenarios. These scenarios represent a wide range of future states of the world and be mutually exclusive and collectively exhaustive so that probabilities can be assigned to them. This enables us to compute values for the new technologies across a wide range of possible technological and socio-economic futures. Figure 3 shows the key elements of the technology evaluation system.

**Figure 3.** Schematic Diagram of Technology Evaluation Process
We are designing these scenarios to be as informative as possible about the efficacy of the GCEP R&D portfolio. For example, they range from a (relatively low probability) case where there is no future concern about climate change to one in which (say twenty years from now) where climate change is perceived to be a (relatively low probability, but plausible) much more serious problem than currently expected. In the former case, only a small number of low-/non-carbon emitting technologies (e.g., perhaps advanced-technology combustion engines) will be adopted, whereas in the latter many low-/non-carbon emitting technologies that are more expensive than conventional carbon emitting technologies will be adopted. This comparison illustrates the “option value” associated with the development of new technologies. If new technologies are developed they can be introduced and diffused if they are needed, but kept “on the shelf” (and perhaps put into further development to make them more economical) if they are not needed.

The valuation model will also evolve over time from a simple two sector, five region specification with sensitivities on parameter values to a more sophisticated system with greater detail and inputs calibrated to more complex models, estimated from primary data and/or obtained via expert assessments. Uncertainty about the cost and performance of the technology being evaluated, and of the technologies with which it might compete are initially being represented by sampling from probability distributions over those characteristics. Over time more sophisticated ways of incorporating the actual probability distributions into the analysis will be adopted, and the R&D effort will be broken down into stages reflecting the logical technical challenges that need to be met to bring the technology to fruition as well as the option to improve it over time. This information will allow us to look at the optimal R&D portfolio more fully as a sequential decision making problem over time where stages of the R&D on a particular technology may be pursued with subsequent stages either canceled or accelerated depending on how the energy system and the climate problem evolve.

Finally the technologies are to be evaluated in groups in hopes of finding the most valuable portfolio(s) of technology options given the uncertainties about technology costs and performances, scenario variables, and valuation model parameters. Here we will consider using the whole portfolio as a hedge against future uncertainties as well as using individual elements of the portfolio as hedges against lack of technical or economic success in the other elements of the portfolio.

Prototype Valuation Framework

This year we have worked on putting together a prototype valuation model. Although this model is not quite yet ready to be used in the technology assessments, the basic structure seems workable, developing it has revealed a number of challenges that will need to be met to develop a more useful, and some basic insights can be illustrated semi-quantitatively. We start with information regarding the characteristics of the new energy technologies resulting from R&D (expressed via probability distributions over costs and performance at specific future dates of interest as described above). Assessments of the value of that new technology depend on what other new technologies have been developed, how fast existing technologies are improved, and conditions in energy
markets. Thus, these evaluations require a type of “integrated assessment” of all technologies under all possible market conditions. The basic approach pursued in the design of the prototype evaluation system has been initially divide the world up into two parts: (1) what the GCEP Portfolio can provide in terms of supplies of carbon energy substitutes at various price levels, and (2) what the world might demand of this portfolio under a wide range of future energy market futures. Obviously both the technology assessments and market assessments are very complex and highly uncertain.

The preliminary assessment systems starts with a highly simplistic and aggregate representation of key elements, but is designed in a way to which more detailed information from any source can easily be added as necessary (in modeling parlance this framework has been designed to be highly scalable). The value of each individual GCEP research program is evaluated in terms of its contribution to the value of the whole GCEP portfolio which is in turn evaluated in terms of its contribution to key energy sectors in key world regions in the future. A globally aggregated version of this framework is described here in some detail, followed by a description of the level of geographical and sectoral disaggregation, and dynamics currently being incorporated in the prototype assessment framework.

The simplest aggregated version of the framework looks at the GCEP enabled supply and rest-of-world demand for non-carbon energy at various future dates of interest. The supply side of the framework consists of the collection of stochastic GCEP R&D program supply curves described above. Initially these consist of a single subjective probability of technical success of the program and a probability distribution over the cost of employing the new technology commercially.

The demand for non-carbon energy takes into account possible future conditions in the global energy system including the implications of alternative fuel price scenarios, improvements in non-GCEP technologies (through learning over time, with respect to non-GCEP R&D funding, and with respect to cumulative experience), critical materials or infrastructure constraints on the rates of new technology adoption, economic growth rates, structural changes in the global economy, and government policies including those directly related to climate change. Forecasting how all these factors will work towards creating a market for advanced non-carbon technologies is extremely complicated and highly uncertain. But it is just this wide range of possible outcomes that can create a very large value for advanced technology development.

Conceptually one could construct these demand curves for non-carbon energy by taking any of the leading global energy models and for one set of model parameters, one set of model drivers and one set of policies and add a fictitious source of non-carbon energy at a very low price and observe the demand for it, subsequently increasing the price again and again until none is demanded. In this way a demand curve for non-carbon energy for one model implemented state of the world could be developed. Since the focus of GCEP is on long-run pre-competitive R&D to help prepare for a very wide range of future states of the energy system it would be cumbersome and probably infeasible to run a large-scale model thousands of times to develop the demand side of
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the framework. In addition, large-scale models may impose too much structure on the world energy system to be appropriate for this task. Thus, we start with very aggregated energy system models which can be calibrated to the exiting set of large-scale energy models, but also take inputs from a number of other sources including relevant empirical work and expert opinion. This information is also integrated into uncertainty representations (i.e., probability distributions) for demand factors that are similar to the new technology supply uncertainty specifications described above. Given probability distributions for the demand for non-carbon energy in the future and for the supply of each technology included in the GCEP portfolio, stochastic simulation techniques are used to generate thousands of possible supply demand equilibria each including a level of contribution by each technology in the portfolio.

There is a wide range of net benefit measures that could be used to quantify the benefits of the GCEP portfolio for each supply and demand realization. One frequently used metric that is convenient for illustrative purposes here is the increase in net surplus to the economy resulting from the new technologies. For simple supply and demand curves such as those shown in Figure 4 the net surplus gain can be computed as the area under the demand curve less the area under the supply curve. The area under the demand curve represents the total value of the new technologies to consumers and intermediate goods producers while the area under the supply curve represents the total draw on societal resources required to produce the alternative energy. Net surplus is maximized at the point where supply equals demand (also known as the market equilibrium) because to the left of the point the marginal area under the demand curve exceeds the marginal area under the supply curve and that relationship reverses to the right of the market equilibrium point. Using the net benefits triangle is thus easy to calculate the net benefits of the GCEP portfolio for one particular set of technology outcomes and one particular future state of the world energy system. Given the complexities and uncertainties involved though this set of calculations might need to be repeated thousands to millions of times to capture the effect of the full range of outcomes.

Initially this capability will be implemented through Monte Carlo Simulation in which each probability distribution is sampled through the use of appropriate random number generators. For example if an R&D project on a new technology has a .2 chance of demonstrating the technical feasibility of a new carbon free energy technology, a random number between 0 and 1 is generated and the technical demonstration is assumed to be successful if that number is .2 or less and unsuccessful otherwise. Then the cost of the new technology is determined by another random draw used to pick an outcome corresponding to that probability number in the cost distribution for that technology. For example, if .5 is drawn the mean of the probability distribution over future costs is selected. The process is repeated over all the uncertainties many times over to generate probability distributions over various output measures, including the net benefits of whatever portfolio is being analyzed.
As a simple example of this methodology consider the case where world energy demand is aggregated and there are only four technology areas in the GCEP portfolio – solar, wind, biomass and carbon sequestration. The distribution of benefits for the solar technology alone is shown in Figure 5.

Although the most likely level of benefits for this technology is slightly negative (i.e., R&D expenditures and no benefits) reflecting an assumed probability of technical success of .3, there is a substantial probability of annual benefits of $20 Billion per year and relatively small probabilities (tenths of a percent) for benefits all the way up to about $250 Billion per year. These very large benefits occur when the cost of the new technology is very low and the demand for it very high because of, e.g., high baseline carbon emissions, high fossil fuel prices, poor success in the development of other alternative sources of energy by GCEP or anybody else, and a high policy induced financial penalty on carbon emissions.
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Figure 6 shows results for another example portfolio consisting of solar, wind, biomass, and carbon sequestration technology research programs. This collection of technology programs is referred to as a “mini” portfolio because although it includes 4 technology programs they are drawn from only 2 of the 11 GCEP areas. Here the payoff is higher but not dramatically higher because this is substitution between the payoffs of the different elements of the portfolio. There is also much less chance of a negative payoff which results from diversification: that is, the probability of all four technologies proving to be technically infeasible (about .2) is much less than any individual technology program proving to be infeasible. Finally the probability of very large benefits is larger (about .5 to 1.0% for annual benefits $240 Billion or more) as it is better to have two or more chances at a technically feasible and relatively low cost carbon free technology than only one when the demand for carbon free energy is high due to fuel market conditions and public policies.

A More Realistic Prototype Framework

Although useful for illustrating the basic concepts of the technology evaluation framework, the highly aggregated system described above, it is not very realistic because it ignores important regional and sectoral characteristics as well as the dynamics of new technology introduction and diffusion that can have significant impacts on the value of the GCEP portfolio. However, detail needs to be added to the system carefully and only in ways that focus it better on the assessment objective.
The current prototype divides the demand and supply of non-carbon energy into two sectors – electricity generation and transportation and five regions – US, Europe, Japan, China and India. We may include “other sectors” and “rest of the world” categories, but even that may not be necessary to pick up most of the portfolio benefits. In this implementation we also able to incorporate more realistic representations of technology dynamics and resource supply effects.

Results: Modeling the Transition to a Hydrogen Economy

This year’s work in micro level analysis of technologies focused entirely on models designed to examine implications of a possible transition to a hydrogen economy, or more precisely, of a transition to using hydrogen in place of gasoline as fuel for light duty vehicles. This modeling and analysis was developed jointly for GCEP and for the National Research Council (NRC) “Committee on Alternatives and Strategies for Future Hydrogen Production and Use”. This work was incorporated in the National Academies’ recently published study: The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs.

A complete draft of the National Academies’ study is currently available online at www.nap.edu. A final version of the report will be published and available at that site once the line editing has been completed and the document has been typeset. In this technical report we summarize some of the modeling and analysis developed jointly for
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GCEP and the National Academies’ study. It should be noted that this modeling and analysis included intellectual contributions by all members of the NRC committee and by its consultants, in addition to the contributions by James Sweeney.

The Modeling and Analysis: Summary of Methods

The goal of the modeling and analysis was to develop insights into the implications of moving to hydrogen as fuel for light duty vehicles. But there are still many technical, institutional, regulatory, and economic barriers to the use of hydrogen as an automotive fuel. This modeling and analysis is based on explicit assumptions that an aggressive research and development effort is successful in reducing the costs of proton exchange membrane (PEM) fuel cells, is successful in solving the challenge of on-board storage of sufficient quantities of hydrogen, is successful in developing safety and other regulatory standards. The analysis is based on the assumption that, as a result of the R&D and of the regulatory progress, the total production and maintenance costs of fuel cell vehicles becomes equivalent to that of hybrid vehicles fueled by gasoline, or that any additional costs of such vehicles is matched by increased functionality that vehicle purchasers would find attractive enough to compensate for the additional production and maintenance costs. The work conducted for GCEP does not make a judgment about whether the R&D will be so successful, but rather provides analysis of the implications of such successful R&D.

The modeling and analysis started with mathematical models which build up estimates of the unit costs (costs per kilogram of hydrogen) that could be expected for the various hydrogen-supply technologies. These models are designed to estimate unit costs of the production, transportation, and dispensing of hydrogen for use in automobiles. These models incorporate estimates of the major components of cost, including the capital depreciation and amortization, feedstock costs, costs of electricity or other energy inputs, costs of separating carbon dioxide from the gas stream, costs of sequestering carbon dioxide, and operations and maintenance costs. Consistent assumptions about economic conditions, interest rates, electricity costs, and carbon prices (if any) are used across the various technology estimates. These models were first developed by SFA Pacific to be used by the NRC committee. They were subsequently modified as a result of deliberations by the NRC committee members.

The unit cost models are available in two versions. The first includes estimates of costs that would be incurred if current technologies were utilized. The second version includes estimates of unit costs, conditional upon technological advances. The latter version depends on the technological judgments of the members of the NRC “Committee on Alternatives and Strategies for Future Hydrogen Production and Use”.

Linked to this the first group of unit cost models are models designed to examine the quantitative impacts of various technologies if successful. Currently the primary such model is a relatively simple vintage capital representation of automobile use of fuels. The model uses as inputs the assumed fractions of new vehicles in any future year which would be fueled by hydrogen and the assumed fractions of new gasoline-powered vehicles that are hybrid vehicles or conventional vehicles. This model then keeps track of
the projected number of vehicles produced in any year, the capital stock of automobiles from the various vintages, the average fuel efficiency of each vintage, the fraction of vehicles from each vintage that would be fueled by hydrogen as opposed to gasoline, the assumed differential fuel efficiency of new hydrogen vehicles, the growth of vehicle miles traveled, and the resulting consumption of hydrogen and gasoline.

In addition, these consumption estimates have been combined with estimates of carbon dioxide emissions from gasoline-based consumption and the carbon dioxide emissions from the various hydrogen-producing technologies in order to estimate how implementation of various hydrogen production technologies might decrease or increase the emissions of carbon dioxide into the atmosphere and the quantities out of carbon dioxide sequestered.

Similarly, based on estimates of the unit cost of producing hydrogen from various technologies, the model are used to provide quantitative estimates of changes in the total cost of fuel for vehicles, conditional on implementation of the various hydrogen-production technologies. For the NRC study, these unit costs are based on the unit cost models described above.

Finally, these models are used to estimate quantities of other resources that would be used to produce the hydrogen. Estimates currently have been developed for use of natural gas, coal, and land, conditional on various technological pathways for hydrogen production. In addition, for scenarios in which carbon dioxide is separated and sequestered, the annual quantities and cumulative quantities of sequestered carbon are estimated.

Results Included in the National Academies’ Hydrogen Study

In what follows are graphical summaries of results of the modeling and analysis, as included in the National Academies’ recently published study: The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs. The interested reader can read more detailed discussions of these results in that study, currently available online at www.nap.edu.

Figure 7 shows the estimated unit costs of the various technologies, based on currently available state of technology. The heights of the bars represent the unit costs, expressed as dollars per Kg of hydrogen. The four bars on the left are all central station technologies (CS), large enough to produce 1.2 million Kg of hydrogen per day, roughly enough to fuel 2 million light duty vehicles from each such plant. Two use coal as a feedstock (Coal) and two use natural gas (NG). For one coal and one natural gas technology carbon dioxide is separated and sequestered (Seq); for the other two technologies carbon dioxide generated during the production process is vented into the atmosphere (No label). The two bars in the center are all mid-size (MS) technologies, large enough to produce 24,000 Kg of hydrogen per day, roughly enough to fuel 40 thousand light duty vehicles from each such plant. They use biomass (Bio) as a feedstock, which is gasified for producing hydrogen.
The next four bars are distributed (Dist) technologies, large enough to produce 480 Kg of hydrogen per day, roughly enough to fuel one thousand light duty vehicles from each such station. The first of these distributed technologies is a small reformer, using natural gas as a feedstock. The other three use electrolyzers, in which electricity is used to dissociate water, producing hydrogen and oxygen. One of these three is based on electricity taken from the grid; such electricity is represented as being generated by mix of primary energy sources typical of the U.S. grid. The second is based on two sources of electricity: electricity is generated from wind turbines (WT) during the time sufficient electricity is available from these turbines; electricity is taken from the grid at all other times. The third is also based on two sources of electricity: electricity is generated from photovoltaic (PV) cells during the time sufficient electricity is available from these PVs; electricity is taken from the grid at all other times\(^1\).

The final bar represents gasoline, expressed in a per-mile hydrogen-equivalent basis. This bar represents the cost to produce enough gasoline to drive one hybrid vehicle the same number of miles as a fuel cell vehicle can be driven using one Kg of hydrogen. In this discussion, that will be referred to as the “per-mile hydrogen equivalent” gasoline cost. This gasoline cost is based on nation-wide U.S. estimates, for crude oil prices of

\(^1\) We also examined electricity derived entirely from wind turbines or from photovoltaic cells, not using grid electricity as a backup. However, these would require substantially larger electrolyzers, since the electrolyzer would be operating only a small fraction of the time. The increased capital cost of the larger electrolyzer leads to significantly greater unit costs than those pictured in this graph.
$30 per barrel. This estimate is very sensitive to the assumptions about the future price of crude oil.

In Figure 7, five different components of costs are presented for the central station and the mid-size technologies: production, distribution by pipeline or truck, dispensing, CO₂ disposal (sequestration), and “carbon imputed cost”. The “carbon imputed cost” is an estimate of environmental cost of carbon dioxide release, based on an assumed environmental cost of $50 per tonne of carbon. However, for the distributed station, the production and dispensing cost are modeled as being part of one integrated operation; there is no distribution cost because the hydrogen is produced on site. Thus only the total distributed cost and the “carbon imputed cost” are included for these technologies.

Figure 7 indicates that even with current technologies, if the U.S. were to have large enough hydrogen production plants, it would be possible to produce hydrogen using either coal or natural gas as a feedstock, at delivered unit costs that would be very similar to unit costs (on a per-mile hydrogen equivalent basis) of using gasoline in hybrid vehicles. This implies that if the challenges of producing fuel cell vehicles were solved, so that these vehicles had production and maintenance costs equivalent to these costs for hybrid vehicles, then at a large scale of hydrogen production the fuel costs for fuel cell vehicles would also be very similar to fuel costs for hybrid vehicles. Thus such vehicles could be competitive with hybrid vehicles.

Figure 7 also indicates that unless technologies are improved from the current technologies, hydrogen produced from renewable energy or by electrolyzing water would be substantially more expensive than hydrogen produced from fossil fuels.

More detailed cost estimates are shown in Figure 8 for the same current technologies. In this figure, the production costs are further broken down into several cost components: capital charges, feedstock costs, electricity cost, non-fuel operations and maintenance (O&M) and fixed costs. These categories are also shown for the distributed hydrogen production technologies.

Figure 8 shows that for hydrogen generated using electrolysis, the cost of electricity is the most important cost element, followed by capital costs, primarily capital costs of electrolyzers and of storage facilities. Capital costs are large components of the cost of biomass. In addition, distribution costs of these mid-size facilities are large, since distribution by pipeline increases sharply on a per-unit basis for these smaller facilities. Distribution by truck seems to be the lowest cost option.
We have developed similar cost estimates for potential future technologies. These estimates were based on the technical judgments by the members of the NRC “Committee on Alternatives and Strategies for Future Hydrogen Production and Use”. They are meant to represent moderately optimistic judgments about the improvements in these technologies, if an aggressive R&D program is directed toward the technologies and is successful. Figure 9 presents these cost estimates, using the same scale as used in Figure 7. Only one new technology is introduced: nuclear energy (Nu) in a reactor run at high enough temperatures to cause direct dissociation of hydrogen from oxygen in water.

Figure 9 shows that with technological advances, hydrogen could be generated from fossil fuels, distributed, and dispensed to the consumers at costs lower than the costs of gasoline (with $30 per barrel crude oil prices.) Cost of hydrogen from wind-turbines, from distributed natural gas reforming, and from nuclear power would be more expensive than gasoline costs, but not very much more expensive.

The potential future generation of hydrogen by electrolysis, using wind turbines for the electricity is based on the wind turbines being used to provide all of the electricity. If the cost of fuel cell stacks drop sharply, then costs of electrolyzers are likely to drop sharply as well. Such a change would make low quality, intermittent electricity economically attractive for electrolysis: it would be more economical to invest in large electrolyzers and to use them only when the wind turbines are generating electricity.
Gasification of biomass and electrolysis from grid-derived electricity or from photovoltaics is expected to be substantially more expensive, even with the technology advances we have postulated.

More detail on these cost estimates is provided in Figure 10. This figure shows that the high cost of electricity is expected to be the dominant factor in the unit costs of electrolysis-based hydrogen production. It shows that the high costs of distribution of hydrogen from mid-sized plants is a key factor, but not the only factor, in the high unit costs of biomass gasification. This suggests that methods of reducing this cost, say through a network of pipelines that could connect mid-sized plants could significantly reduce these cost estimates.

Additional discussion of these cost estimates is provided in the National Academies’ recently published study: *The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs.*
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Possible Future Technologies: Cost Estimates

Figure 10. Details of Unit Cost Estimates for Possible Future Technologies

Unit estimates of carbon releases into the atmosphere from light duty vehicles are provided in Figure 11 for currently available technologies and in Figure 12 for possible future technologies.

These graphs suggest none of the technologies would increase the unit emissions of carbon dioxide into the atmosphere above the amounts that would be associated with use of gasoline in hybrid vehicles. Technologies involving capture and sequestration of the carbon dioxide could sharply reduce the unit releases of carbon dioxide. Generation of hydrogen through electrolysis could reduce unit emissions, but for current technologies the reduction would not be very large. However, with potential future technologies, use of wind turbines could reduce emissions to zero, since in this case no grid-based electricity would be used. Use of natural gas could reduce emissions, but again, not by large amounts, absent carbon dioxide sequestration.
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Current Technology Estimates: Carbon Released to Atmosphere

Possible Future Technology Estimates: Carbon Released to Atmosphere

Figure 11. Unit Estimates of Carbon Releases for Currently Available Technologies

Figure 12. Unit Estimates of Carbon Releases for Possible Future Technologies
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Biomass technology is particularly interesting from a carbon management perspective, if the carbon dioxide is separated and sequestered when the biomass is gasified. In that case, only a very little carbon dioxide would be released into the atmosphere at the point of gasification. None would be released at the point of use. However, growing of the biomass would take carbon dioxide out of the atmosphere. Most of this carbon dioxide would be sequestered. Thus, on net, use of biomass could reduce the amount of carbon dioxide: on net it could lead to negative emissions of carbon dioxide, if the carbon dioxide were separated and sequestered.

The unit estimates discussed above were incorporated into a vintage capital model of the light-duty vehicle evolution over time in order to create several quantitative scenarios of the introduction and growth of hydrogen use in light duty vehicles. We turn now that discussion.

As discussed above, the analysis assumes that the maintenance and production costs of fuel cell vehicles can be made equivalent to the costs of hybrid vehicles. In order to meet this end, fuel cells would need very large improvement from their current state. In particular, it would be necessary to meet cost targets for the fuel cell stack of about $50 per KW. The stacks would need much longer lives than is now the case, on the order of 4,000 to 5,000 hours of operation over the normal lifetime of a passenger car. On board storage of hydrogen must be improved in order to provide an adequate range between refuelings, on the order of 300 miles. In what follows, in some scenarios we assume all these goals have been met.

We have developed three scenarios in order to estimate quantitatively the impacts of fuel-cell vehicles. The first scenario, perhaps the most unlikely, is one in which the goals are not met, so that hydrogen vehicles are never introduced in large scales. In addition, in this scenario hybrid vehicles never command a large market share, so that almost all of the vehicles remain conventional gasoline-fueled light duty vehicles.

The second scenario is also one in which the goals are not met, so that hydrogen vehicles are never introduced in large scales. But in this scenario hybrid vehicles grow steadily in market share, ultimately replacing all conventional vehicles.

The third scenario is one in which the fuel-cell vehicle goals are met and hydrogen progressively becomes the dominant fuel for light duty vehicles. In this scenario, hybrid vehicles first replace conventional vehicles over time; then H₂ vehicles replace hybrid vehicles. The number of conventional vehicles follows same time trajectory whether or not hydrogen vehicles are successfully introduced.

The second and third scenarios allow the comparison between a successful introduction of hydrogen fuel cell vehicles and no successful such introduction. The first scenario provides a baseline for projections of the current system.
The analysis depends on assumptions about the changes over time in the fuel efficiency of the three types of vehicles. We assume that in each scenario the fuel efficiency of conventional vehicles again begins to grow. We assume that hybrid vehicles have a 45% gain in fuel efficiency over conventional vehicles and that fuel cell vehicles have a 66% gain over hybrids. Figure 13 shows the assumed fuel efficiencies over time, measured in miles per Kg of hydrogen or miles per gallon of gasoline, of the fleet of new light duty vehicles. Note that these estimates include not just small vehicles, but a mix of differing weights and sizes of light duty vehicles.

![Figure 13. Fuel Economy Over Time Assumed for Three Vehicle Technologies](image)

Figure 14 shows the assumed penetration rates of the new vehicles in the second and third scenario. (In the first scenario there is no penetration of either hybrid or fuel cell vehicles.) In the second scenario, hybrid vehicles increase to 100% market share of new vehicles and conventional vehicles decrease to zero market share by 2035. In the third scenario, the growth of hybrids is interrupted by the rapid growth of hydrogen fuel cell vehicles, which increase to 100% market share before 2040.

The entire inventory of vehicles on the road adjusts only with a lag to the adjustments in new vehicle sales, since in any year, the inventory is dominated by previous vintages of vehicles. Figure 15 provides estimates of the on-the-road inventory of vehicles, using a very simple vintage capital model of the vehicle fleet.
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![Assumed Fractions of New Vehicles](image1)

**Figure 14.** Assumed Fractions of New Vehicle Types: Three Scenarios

![Assumed Fractions of Vehicle Fleet](image2)

**Figure 15.** Estimated On-the-Road Fractions of Vehicle Technologies
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Figure 14 and Figure 15 represent an optimistic assessment of the rate at which new fuel cell vehicles can penetrate into the market and the rate at which the fleet of vehicles would evolve. They show that if hydrogen technologies are successful, the evolution of the system would occur only over many decades, converging to 100% market share of hydrogen vehicles no earlier than about 2050.

In order to determine the consumption of gasoline and of hydrogen in the various scenarios, it is also necessary to estimate how much vehicles would be driven, the vehicles miles of travel. We assumed that the total vehicle miles would increase by 2.3% per year over the time horizon. The assumed trajectory of vehicle miles traveled is shown in Figure 16.

![Vehicle Miles Travelled (Billions)](image)

Figure 16. Assumed vehicle miles of travel (Growing 2.3% per year)

The assumptions described above lead to projections of gasoline use over time in the three scenarios. These estimates are shown in Figure 17. This figure shows that absent either hybrid vehicles or hydrogen fuel cell vehicles gasoline consumption would steadily increase over time. The second scenario shows that a market shift toward hybrid vehicles could stop the growth of gasoline consumption, at least temporarily. However, if hydrogen fuel cell vehicles were to follow the diffusion pattern of scenario three, then by 2050 consumption of gasoline would be completely phased out.
As gasoline consumption is decreased in the third scenario, hydrogen consumption would be increased over time. Figure 18 shows the projected increase in hydrogen consumption over time, if hydrogen fuel cell vehicles penetrate the market consistently with the third scenario.

Figure 18 shows that it would be not until about 2027 that hydrogen use for light duty vehicles would be as large as the current U.S. production of hydrogen. However, by 2050, the use of hydrogen for vehicles could increase to over 100 billion Kg per year, or over 100 billion tons of Kg per year.

In what follows, it will be assumed that the hydrogen production and use for light duty vehicles follows the growth path of Figure 18.

However, various pathways are possible for producing the hydrogen, including each of the technologies shown in Figure 7 and Figure 8. In order to examine the implications of the various technologies, impacts of moving to a hydrogen economy are examined under the assumption that all of the hydrogen is produced using a single technology. The graphs in the subsequent portion of this report are based on 100% of the hydrogen being generated from a single technology.
In fact, moving toward a hydrogen economy would not lead to all hydrogen production being based on a single technology. It is more likely that a mix of technologies would be utilized. In that case, the various impacts would be based on a weighted average of the impacts estimated for the various single technology scenarios.

We turn now to an examination of the impacts of hydrogen technologies on carbon dioxide released into the atmosphere.

Under these assumptions, the transition to hydrogen could greatly influence the emissions of carbon dioxide into the atmosphere. If no hydrogen were introduced into the system, but hybrid vehicles grew in market share consistently with scenario two, the emissions of carbon dioxide into the atmosphere would increase until the year 2010 and would then remain roughly constant through the year 2040. This is shown by the orange curves in Figure 19 below.
Figure 19. Carbon Releases into the Atmosphere from Light Duty Vehicles: Hydrogen Produced from Fossil Fuels
Figure 19 shows carbon dioxide releases for the current technologies and the possible future technologies, (upper panel and lower panel, respectively), for fossil-fuel based production of hydrogen plus hydrogen generated from direct thermal dissociation of hydrogen in a nuclear plant.

For both the current technologies and the possible future technologies, generation of hydrogen using natural gas can significantly reduce the carbon dioxide emissions. Emissions could be sharply reduced by capturing and sequestering the carbon dioxide. Generation of hydrogen from nuclear facilities would even further reduce the emissions.

Figure 20 shows emissions of carbon dioxide for hydrogen made with renewable energy – biomass, photovoltaics, wind turbines – and hydrogen electrolyzed using grid-based electricity. Carbon dioxide releases would be reduced if hydrogen were generated using photovoltaics, wind turbines, nuclear power, or biomass. However, using grid-based electricity to when the wind turbine or photovoltaics was not producing electricity would reduce the degree to which these technologies reduce the carbon dioxide releases.

This graphs show the dramatically negative releases of carbon dioxide from use of biomass when, after the biomass is gasified, the carbon dioxide is separated and sequestered.

We have also examined the impacts of the various hydrogen pathways on the use of other natural resources.

Figure 21 shows the amounts of natural gas that would be used by the various technologies that use natural gas as a feedstock. This graph also plots the projections, to the year 2025, from the Energy Information Administration, of natural gas production, consumption, and exports, not counting use for hydrogen production. The large amount of natural gas that would be needed for hydrogen production could not be supplied from domestic resources. These quantities would likely lead to increased imports of natural gas.

This impact can be quantified by comparing the reductions in oil use – and hence oil imports – with the increase in natural gas consumptions – and hence imports. These comparisons are shown in Figure 22, for potential new technologies. A graph based on potential future technologies would look very similar. This graph shows that, on an energy equivalent value, the increases in natural gas imports would be very similar in magnitude to the reductions in oil imports. Such a shift cannot be expected to contribute to energy security.
Figure 20. Carbon Releases into the Atmosphere from Light Duty Vehicles: Hydrogen Produced Using Current Non-Fossil Fuel Technologies
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**Figure 21.** Natural Gas Used to Generate Hydrogen: Current and Future Natural-Gas-Based Technologies

**Figure 22.** Impacts on Gasoline Use vs Natural Gas Use: Possible Future Technologies
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For hydrogen generation using coal, however, the results are quite different. Figure 23 shows the amount of coal that would be used if all of the hydrogen were produced from coal. The EIA projections of U.S. coal production and use are also plotted on the same graph. Although coal used for hydrogen production could be a significant fraction of the projected use of domestic coal, this increase in production could be satisfied from domestic coal production.

![Coal Used to Generate H2](image)

**Figure 23. Impacts on Coal Use: Current and Future Technologies**

If biomass were used as the feedstock, then it would be necessary to grow the biomass. Figure 24 provides estimates of the amount of land that would be required if all of the hydrogen were produced using biomass. This suggests that 300,000 to 600,000 square miles of land would be needed to produce all the hydrogen from biomass. In order to put this in perspective, it can be noted that the U.S. currently uses 700,000 square miles of land as crop land and 900,000 square miles of pasture land. This suggests that, although one could use biomass to produce some hydrogen, it would not be viable to use it as the primary source of hydrogen.
The final natural resource examined is sites for sequestration of carbon dioxide. Figure 25 shows the annual amount of carbon dioxide that would be sequestered for those technology pathways that involve sequestration. Shows the cumulative amount of carbon dioxide that would be sequestered. These suggest that between 0.8 and 1.6 billion metric tonnes would be sequestered annually, leading to a cumulative amount sequestered by 2050 of between 10 and 20 billion metric tons. Much research is still needed to ascertain the amount of carbon dioxide that could be safely sequestered. However, for perspective, it can be noted that the estimated capacity of depleted U.S. oil and gas reservoirs is between 25 and 50 billion metric tonnes. In unminable U.S. coal seams there is an estimated capacity to sequester carbon dioxide of 15 billion metric tonnes.
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Figure 25. Annual Amount of Carbon Dioxide Sequestered: Future Technologies

Figure 26. Cumulative Amount of Carbon Dioxide Sequestered: Future Technologies
Finally is the issue of cost for the supply of fuel for the nation’s fleet of light duty vehicles. Using the unit cost estimate in combination with estimates of the rate of introduction of hydrogen vehicles allows estimation of the total costs to the fuel system. These estimates appear in Figure 27 through Figure . Figure 27 and Figure 28 provide estimates for hydrogen produced from fossil fuels, while Figure 29 and Figure provide estimates for hydrogen produced with renewables.

With current technologies, distributed generation of hydrogen from natural gas would remain less costly than use of gasoline in conventional vehicles until the late 2030s. By 2030, without new technologies, the size of the hydrogen market would have increased enough that the cost of distributed generation of hydrogen using natural gas would exceed even the cost of gasoline in conventional vehicles. However, with the potential new technologies, all of the fossil fuel sources of hydrogen would result in a total fuel system cost less than would be the cost of gasoline used in conventional vehicles. Total costs would be similar to costs of the system if hybrid vehicles came to dominate the market.

On the other hand, hydrogen from electrolysis based on renewables or grid-based electricity, or hydrogen from biomass, would lead to sharp increases in the entire fuel system cost with current technologies. (See Figure 29) Even with the potential new technologies (Figure ) most hydrogen production using renewables would be more expensive than the use of gasoline in conventional vehicles and substantially more costly than the use of gasoline in hybrid vehicles.
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Figure 27. Fuel Costs for Light Duty Vehicles: Current Fossil-Fuel-Based Technologies

Figure 28. Fuel Costs for Light Duty Vehicles: Possible Future Fossil-Fuel-Based Technologies
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Figure 29. Fuel Costs for Light Duty Vehicles: Current Non-Fossil-Fuel-Based Technologies

Figure 30. Fuel Costs for Light Duty Vehicles: Potential Future Non-Fossil-Fuel-Based Technologies
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Publications


References


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