

## A Computational Model of Catalyzed Carbon Sequestration

Harrell Sellers\* and Michael Perrone\*  
IBM Research, Yorktown Heights, NY  
sellers@us.ibm.com and mpp@us.ibm.com

and

Raymond Spiteri  
University of Saskatchewan, Saskatoon, SK, Canada

### Summary

This research explores the feasibility of catalysis-based carbon sequestration by efficiently and accurately modeling the underlying chemical reactions and using this model to identify optimal operating conditions. We employ established and novel computational methods to calculate the Arrhenius rate constants required to model the chemical reactions as a coupled system of differential equations and implement this model for carbon sequestration over a palladium catalyst. This approach allows us to explore the behavior of the system for a variety of temperatures, pressures, feed-gas compositions, and catalysts and thereby optimize the amount of carbon sequestered. We discuss trends in the distribution of reaction products as a function of these variables. Preliminary results for this system and previously published results for similar systems indicate that this method can be scaled to accurately predict the efficacy of such systems for carbon sequestration.

### Introduction

Growing international concern over the role of greenhouse gases (mainly carbon dioxide and methane) in global warming has led to increasing pressure for “clean” technologies to reduce the carbon footprint of various industries. A variety of methods have been proposed, and some are beginning to be adopted – most notably geological sequestration – but none of these methods is without drawbacks. It is therefore critical that researchers continue to explore alternative methods for sequestration of greenhouse gases to help find the most cost effective methods possible.

Most carbon sequestration methods are capture-and-storage techniques. In capture-and-storage methods, atmospheric carbon, usually carbon dioxide, is captured, often employing differential adsorption techniques or membrane technologies, and then stored underground in caverns or porous rock or dissolved in the oceans. Some capture-and-storage technologies (mineral sequestration) seek to make limestone, calcium carbonate, or magnesium carbonate, which exist in large quantities in the environment naturally. Geologic sequestration techniques, which are popular at present, store carbon dioxide in geologic structures such as caverns and porous rock. Primary concerns regarding geologic storage include leakages from the storage field, the expense of monitoring and maintaining the storage field for extremely long periods of time, land lease expense,

injection well drilling expense and maintenance, public objection to being in proximity of a storage field of a toxic gas that may leak, and the expense of developing the technology to treat a leaking storage field.

In this paper we describe a computation-based investigation into strategies for the removal of carbon dioxide and methane directly from the point of emission, a process known as *direct carbon sequestration*. We approach this problem using standard and innovative numerical methods to efficiently solve the potentially very high-dimensional systems of differential equation (e.g., models of realistic systems might simulate the evolution of a thousand or more chemical species simultaneously).

In direct carbon sequestration, the chemical inputs must be abundant on-site, and the products must be environmentally benign or have commercial value. For example, carbon dioxide from combustion, atmospheric nitrogen, and methane from coal are readily available at coal-fired electrical generating stations. Generation of thermogenic methane from coal begins in the higher ranks of the high-volatile bituminous coals, and at about 250°F, generation of methane exceeds generation of carbon dioxide. Maximum generation of methane from coal occurs at about 300°F. With even higher temperatures and higher-rank coals, methane is still generated, but at lower volumes [1, 2]. The volatile component of coal can be 15 – 35%, most of which is methane [3]. Thus in the case of coal, direct carbon sequestration appears feasible.

## Theory

The reaction between methane and carbon dioxide yielding soot or graphite and water is thermodynamically favorable [4]:



Hydrogen generation is also possible from a direct carbon sequestration reactor designed for coal-fired electrical generating stations [4]:



Equation 2 above is more thermodynamically favorable than the traditional synthesis gas reaction which runs at 700 – 1000 °C over a nickel catalyst [4]. The temperature of the flue gas at the Otter Tail coal-fired electrical generating station in Big Stone City, South Dakota, is normally between 300–500 °F depending on the electrical load [5]. The temperature of the flue gas is relatively constant from the bottom to the top of the stack due to the relatively high velocity of the exhaust gases. This waste heat can be used to vary the temperature of a catalytic reactor without adding an additional energy expense.

A commercially valuable synthesis gas can also be produced in a direct carbon sequestration reactor:



This reaction is only slightly less thermodynamically favorable than the traditional synthesis gas reaction.

The carbon monoxide produced can be handled in a number of ways. For example, it can be used in synthesis gas applications to produce specialty chemicals, it can be polymerized forming polycarbonate, or it can be further hydrogenated or reacted with carbonaceous radicals on the catalytic surface. Soot or graphite formation is desirable because both forms of carbon sequester essentially just carbon, which could be compressed and shipped back to the coal mine on the coal train's return trip. The synthesis of other commercially valuable chemicals is also possible.

## Method

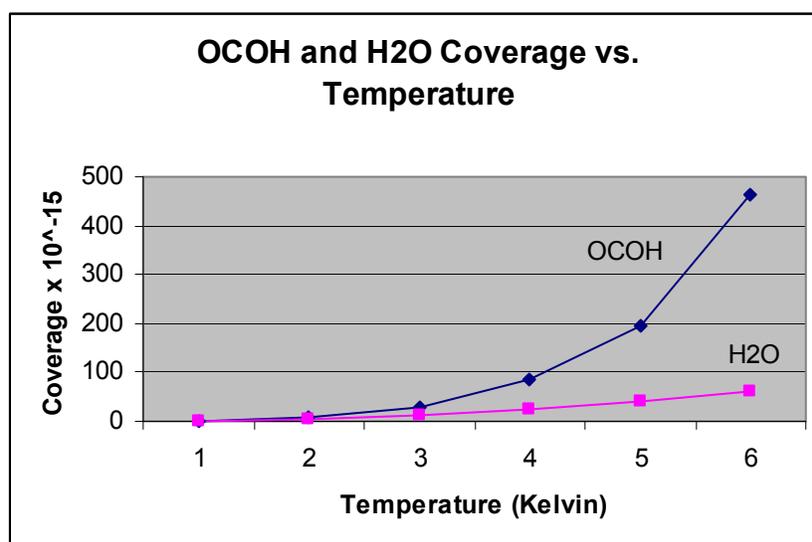
Equation (4) shows the general form of the differential equations that we want to solve where  $C$  is the vector surface concentrations for all of the possible chemical reactants in the system,  $M$  is the matrix of rate coefficients that govern the rate at which any two reactants merge to form a third, and  $N$  is the matrix of rate coefficients for the rate at which individual reactant decompose to create two reactants:

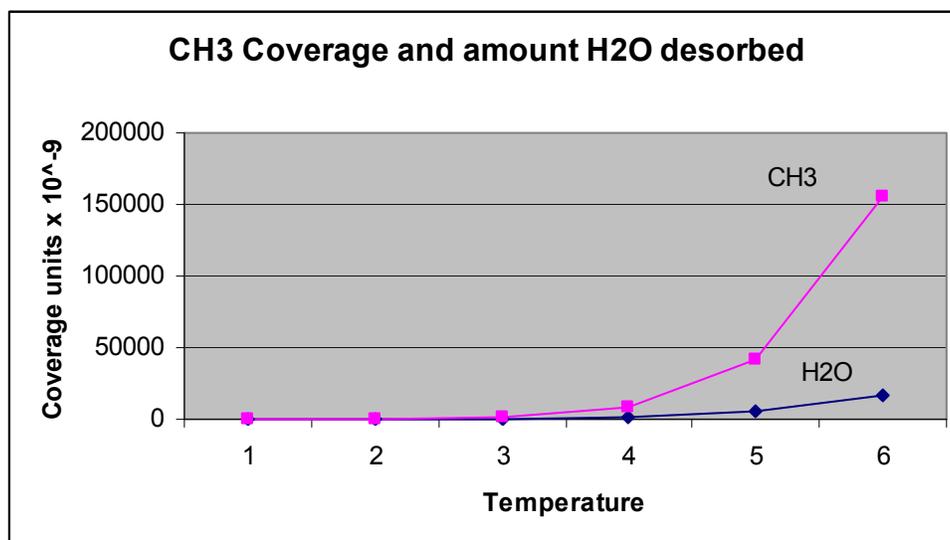
$$\frac{d\vec{c}}{dt} = \vec{c}M\vec{c} + N\vec{c} \quad (4)$$

For this system, we select the reactants that we want to consider in the system, calculate the rate coefficients using methods previously developed [4] and solve the system using a stiff solver to determine the systems capacity for sequestering carbon. The parameters depend on temperature, pressure and the ambient reactant ratios in the surrounding gas. By modifying these parameters we can modify the efficacy of the sequestration.

## Experimental Results

The graphs below display some preliminary results. The first plot illustrates the coverages of OCOH, which is an important reactant intermediate, and water, which is an indicator of the chemistry occurring as a function of temperature. The horizontal axis is temperature in Kelvin beginning at 300 K (approximately room temperature) to 550K in increments of 50 Kelvin. The second plot shows CH<sub>3</sub> coverage and the amount of water that has desorbed. These data were collected after a simulation time of 0.1 microsecond. Data such as these allow us to study the chemical processes that are occurring and make changes in the system to optimize the distribution of reaction products.





## Conclusions

We have proposed a novel approach to perform direct carbon sequestration and have argued that this approach appears feasible for coal-fired power plants. We have described a general mathematical formulation of the problem which is flexible enough to apply to a wide variety of scenarios. We have implemented this formulation and have run computer simulations that demonstrate the kind of behavior we expect from a “bare bones” model of a simple system. We have shown for a small system that the Arrhenius rate constant parameters for a set of chemical reactions on a metal surface can be determined in a timely fashion. In future work, we will scale this problem up to more physically realistic and more complex systems and develop the tools we need to optimize the sequestration efficiency of such systems. We believe that large systems of such equations can be solved efficiently on modern supercomputers to long time-scales, and that these techniques can be applied to model catalyzed carbon sequestration.

## References

1. Rightmire, C.T., 1984., Coalbed methane resources, in Rightmire, C.T., Eddy, G.E., and Kirr, J.N., editors, Coalbed methane resources of the United States: American Association of Petroleum Geologists Explorer, v. 21, no.4 (April, 2000), p. 16, 18-20, 22-23.
2. Rice, D.D. and Claypool, G.E., 1981, Generation, accumulation, and resource potential of biogenic gas: American Association of Petroleum Geologists Bulletin, v. 65, no. 1, p. 5-25.
3. Ramage, J., 1997, Energy: A Guidebook, Oxford, Oxford University Press.
4. Sellers, H., 2007, Modeling the kinetics of large sets of reactions on metal surfaces: Russian Journal of Physical Chemistry B, v. 1, no. 4, p. 377-393.
5. Private communications, Otter Tail Power Company engineering staff of the coal-fired electrical generating station in Big Stone City, South Dakota.