

Technical Progress Report  
"Rate Inhibition of Steam Gasification of Adsorbed Hydrogen"  
DOE Grant #DE-FG22-93PC93213  
Reporting Period: 10/1/94 - 12/31/94

Dennis J. Miller, Principal Investigator

"US/DOE Patent Clearance is not required  
prior to the publication of this document"

Work during the fifth quarter of the grant period has involved both gasification experiments in steam and hydrogen and continued development of the reaction apparatus and analytical methods. Most of the latter work has focused on mass spectrometric analysis of the effluent gases to obtain better response factors and to reduce background signals resulting from impurities in the reacting gas stream.

#### DEVELOPMENT OF APPARATUS AND ANALYTICAL METHODS:

Flow fluctuations: As mentioned in the previous report, we experienced significant, periodic fluctuations in the product gas formation rates and the sample temperature during steam gasification experiments. We determined that these fluctuations were arising from incomplete vaporization of the water feed to the reactor, thus leading to slugs of steam passing through the reactor and subsequent changes in product gas formation rates. We overcame this problem by heating our inlet lines and the exposed end of the high-pressure reactor to higher temperatures. The resulting gasification rates (as seen, for example, in Figure ) are much more stable.

CD<sub>4</sub>/CH<sub>4</sub> Response Ratios: A comparative study of the mass spectrometer responses of CD<sub>4</sub> and CH<sub>4</sub> has been done to investigate the feasibility of using the current calibration gas, which contains CH<sub>4</sub>, as the calibration gas isotopic investigations requiring analysis of CD<sub>4</sub>-containing effluent streams. Response ratios (CD<sub>4</sub>:CH<sub>4</sub>) in pure Argon and 1/3 Ar - 2/3 D<sub>2</sub> have been calculated to be 0.98 and 1.52, respectively. The response ratios calculated at different carrier gas compositions differ enough that response ratios for all carrier gas compositions will be determined experimentally.

Response as Function of Time: An investigation of mass spectrometer response over a five hour period was done to ensure that factors such as background changes and detector drift do not significantly change system responses over time. A five hour interval was chosen because this is about an hour longer than an average experiment. Figure 1 shows two sets of peak heights of each of the three key components of the calibration gas mixture. The peak heights for all species remain almost constant over the five hours, even though Figure 2 shows the major background peak heights change significantly.

Ceramic reactor testing: Experiments in the low pressure ceramic reactor show a significant signal for mass 28 during heatup to 1500°C; this signal makes deconvolution of the CO and CO<sub>2</sub> peaks much more difficult. To address this problem, we followed mass 14 during heatup in an empty reactor and found that, for the most part, it mirrored the mass 28 peak. This indicates that the mass 28 peak contains mainly molecular nitrogen (N<sub>2</sub>). We also found during outgassing of a Saran char sample that similar mass 32, 28, and 44 peaks occurred after several cycles of heatup to 1500°C. The patterns of these peaks, mass 32 up to 350°C, mass 44 predominating from 350-600°C, and mass 28 above 600°C, indicate partial combustion of the carbon is taking place. Together, this information shows that there is a leak somewhere in our reactor system or that argon carrier contains oxygen as

## **DISCLAIMER**

**Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.**

an impurity. We are currently working to identify the source of the leak as either diffusion through the ceramic tube at high temperatures or, more likely, a leak in one of the fittings at the end of the reactor.

Variation of Pressure at Capillary Inlet: Mass spectra of both purge Argon (AGA UHP, 99.999%) and carrier Argon (Matheson UH + 0.9910% Kr) were taken at different gas manifold pressures to characterize the behavior of background species and help identify the source of possible contaminant oxygen in the system. Figure 3 shows total pressure in the mass spectrometer vacuum chamber from both the chamber ion gauge and the mass spectrometer itself as a function of pressure at the upstream end of the inlet capillary tube. The total ion gauge pressure increases with inlet pressure, while the mass spectrometer pressure goes through a maximum as a result of change in detector response with chamber pressure. Figure 4 shows that mass spectrometer background partial pressures of key species also goes through maxima between  $2 \times 10^{-5}$  and  $5 \times 10^{-5}$  torr total pressure. Krypton (mass 84) does not go through a maximum because it is present in a fixed proportion in the carrier Argon. Mass 32 (Oxygen) behaves quite similarly to the other species and has roughly 1/5 the partial pressure of Mass 28 (Nitrogen + small amount CO), which indicates that carrier argons contain no contaminant oxygen but that oxygen and nitrogen together come from a leak in the system.

#### GASIFICATION EXPERIMENTS:

We have conducted a series of steam gasification experiments at 3.3 MPa total pressure, 40% H<sub>2</sub>O/60% argon, and different temperatures to determine the activation energy for gasification and to identify the range of temperatures where transport resistances can be safely avoided. The Arrhenius plot for these five experiments is given in Figure 5; the data show good linearity over the temperature range studied (725 - 850°C) and the calculated activation energy is 47 kcal/mol. This value is somewhat lower than values of 60-80 kcal/mol reported in the literature for steam gasification. We have eliminated the possibility that mass transport limitations are altering the apparent activation energy by calculating the generalized modulus  $\Phi = \eta \phi^2$  for each temperature: values of  $\Phi$  much less than one indicates mass transfer does not significantly influence reaction rate. The largest value of  $\Phi$  observed is  $1.4 \times 10^{-8}$  at 850°C, clearly showing that the measured rates are the intrinsic kinetic gasification rates. Figure 6 shows formation rates of key species in steam gasification at 850°C and 200 psi steam partial pressure during a typical two-hour experiment.

We have initiated D<sub>2</sub> gasification studies on annealed Saran char; rates are comparable to gasification rates in H<sub>2</sub>, but experiments conducted so far have not allowed us to successfully deconvolute CD<sub>4</sub> formation from D<sub>2</sub>O background.

Summary: We have conducted detailed studies during the fifth quarter but made only moderate advances in the overall grant objectives, as a result of attempts to identify and rectify the source of impurities in our system, likely from a leak in the ceramic reactor. We are confident that our measurement techniques are correct and are giving us a good representation of the behavior of the Saran and coal char samples; our ability to reduce background signals during outgassing experiments will make analysis of gas evolution during outgassing much easier and more precise. We hope to quickly rectify problems with gas impurities and move further into core experimental studies.

#### **DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

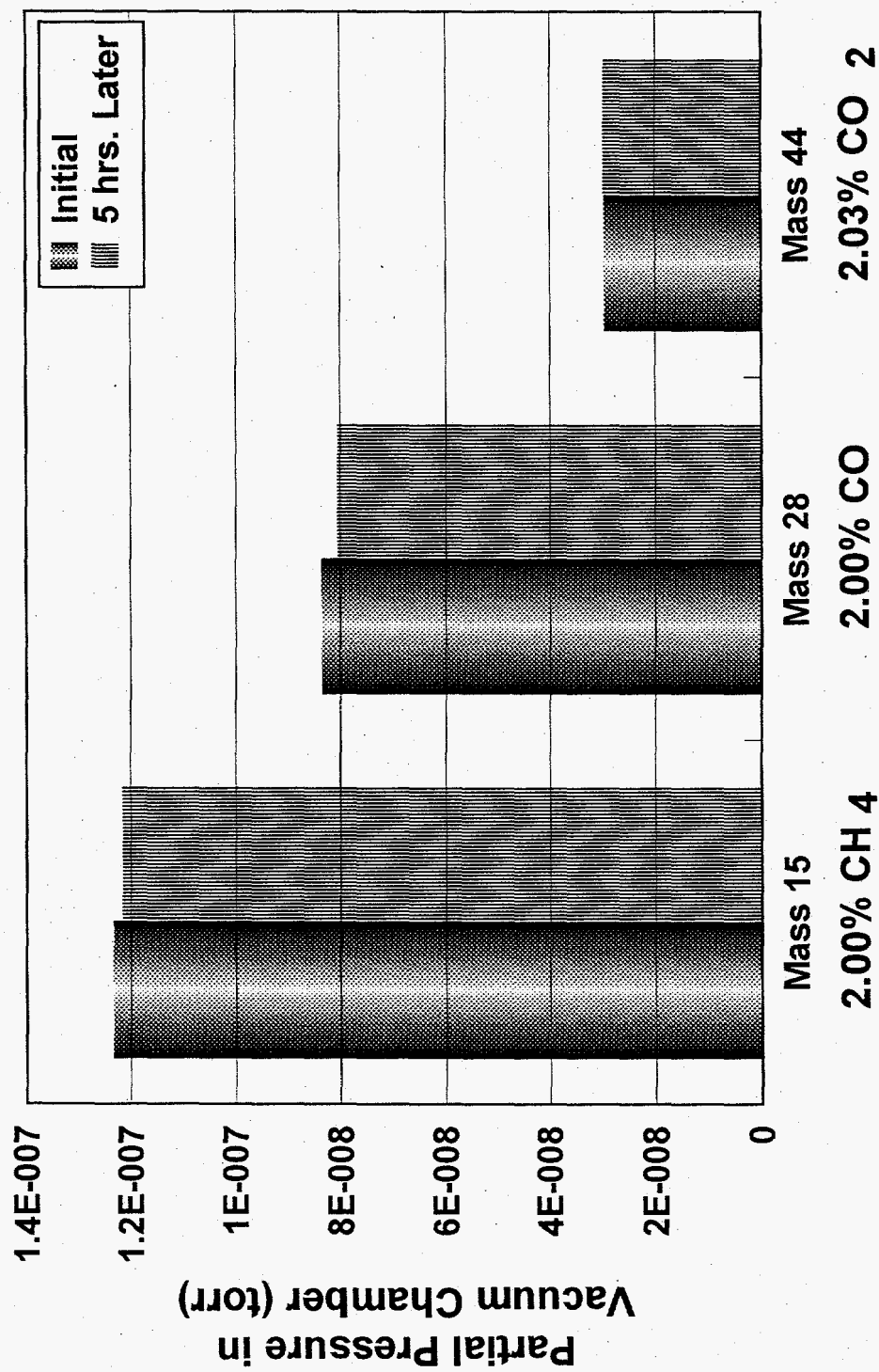


Figure 1: Change in Mass Spectrometer Peak Height of Calibration Gas Key Components over 5hr. Time Interval

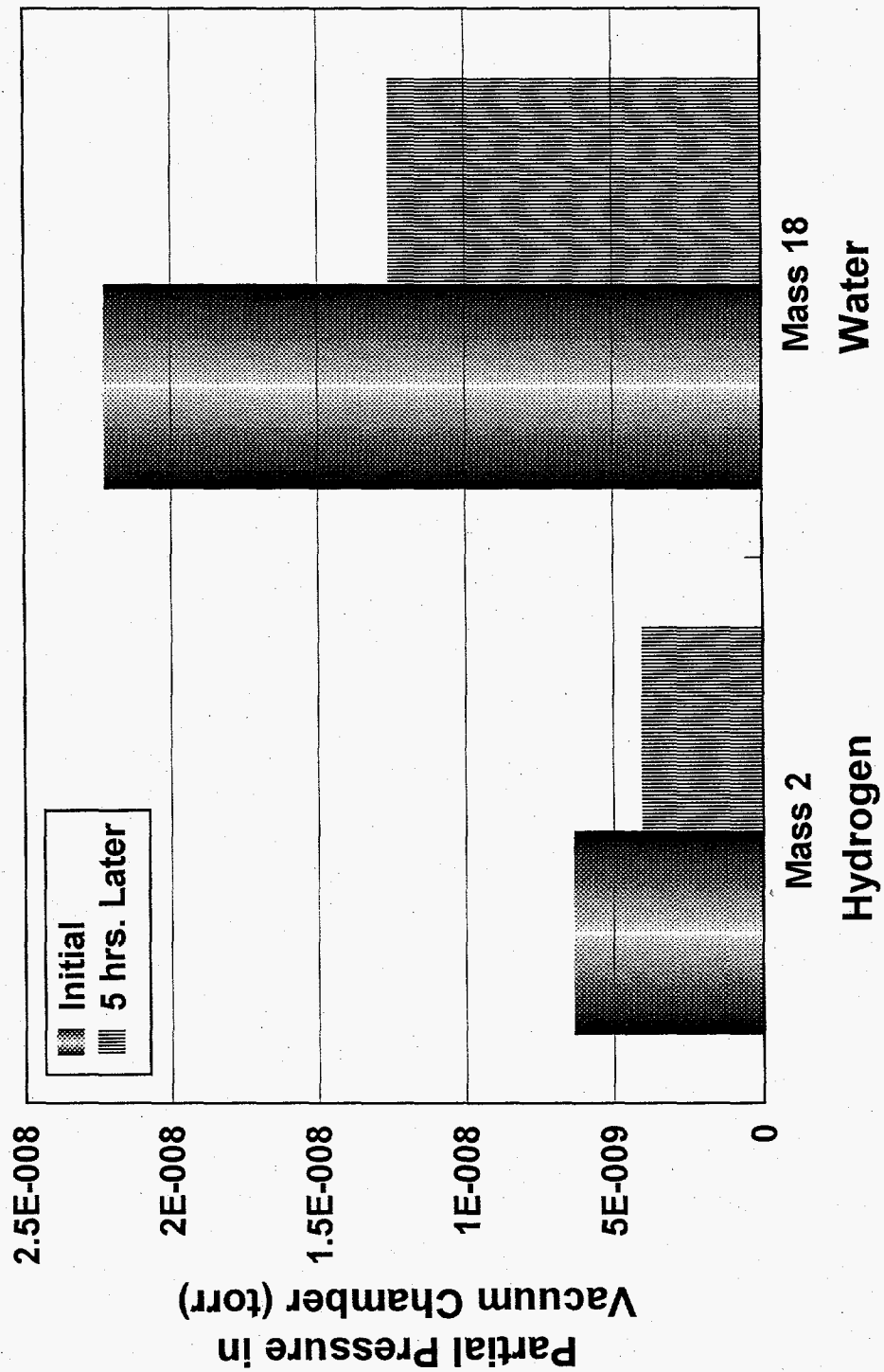
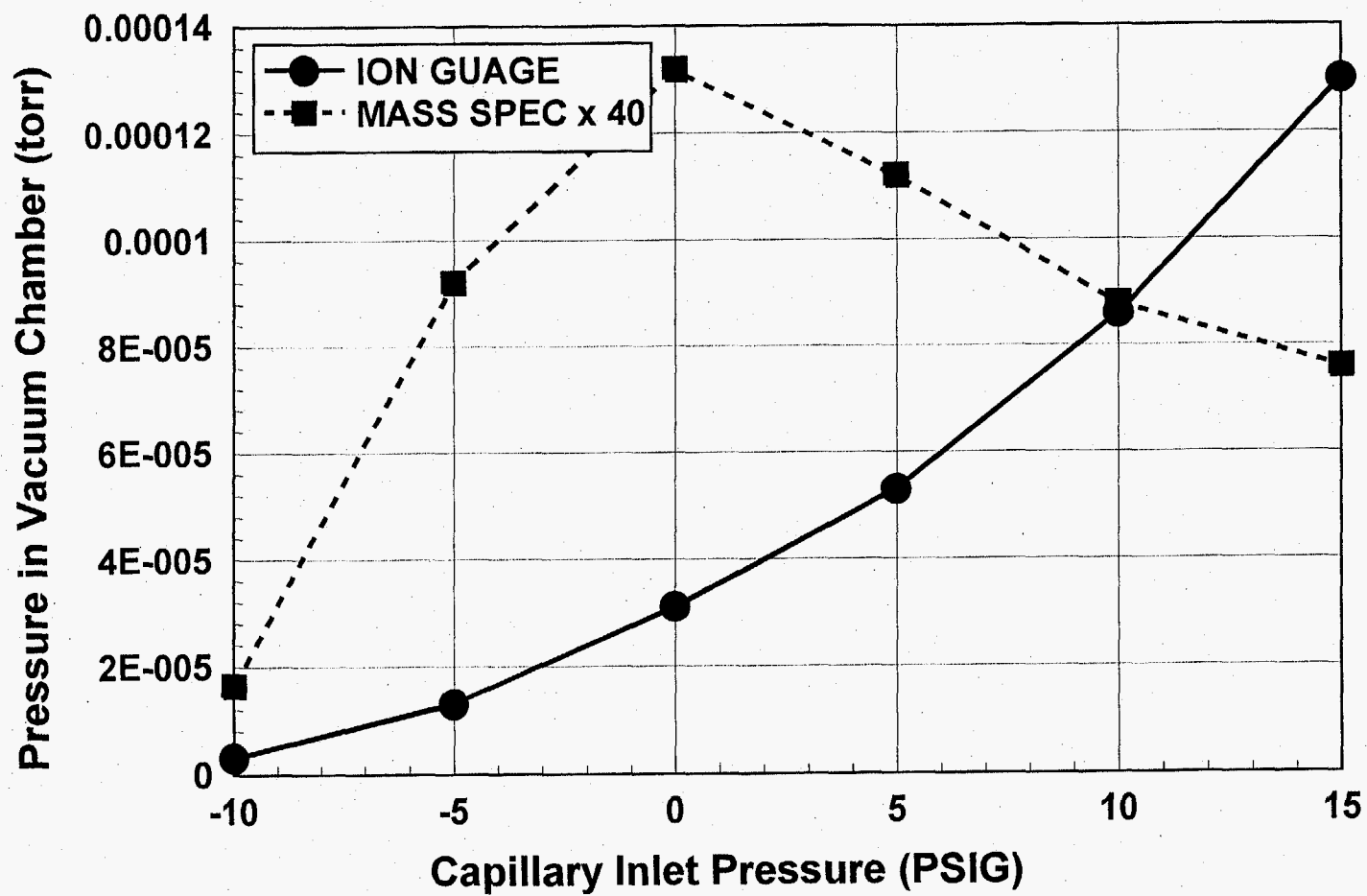


Figure 2: Change in Mass Spectrometer Peak Height of Major Background Species over 5hr. Time Interval



**Figure 3: Pressure in Vacuum Chamber as a Function of Capillary Inlet Pressure (Purge Gas = Argon)**

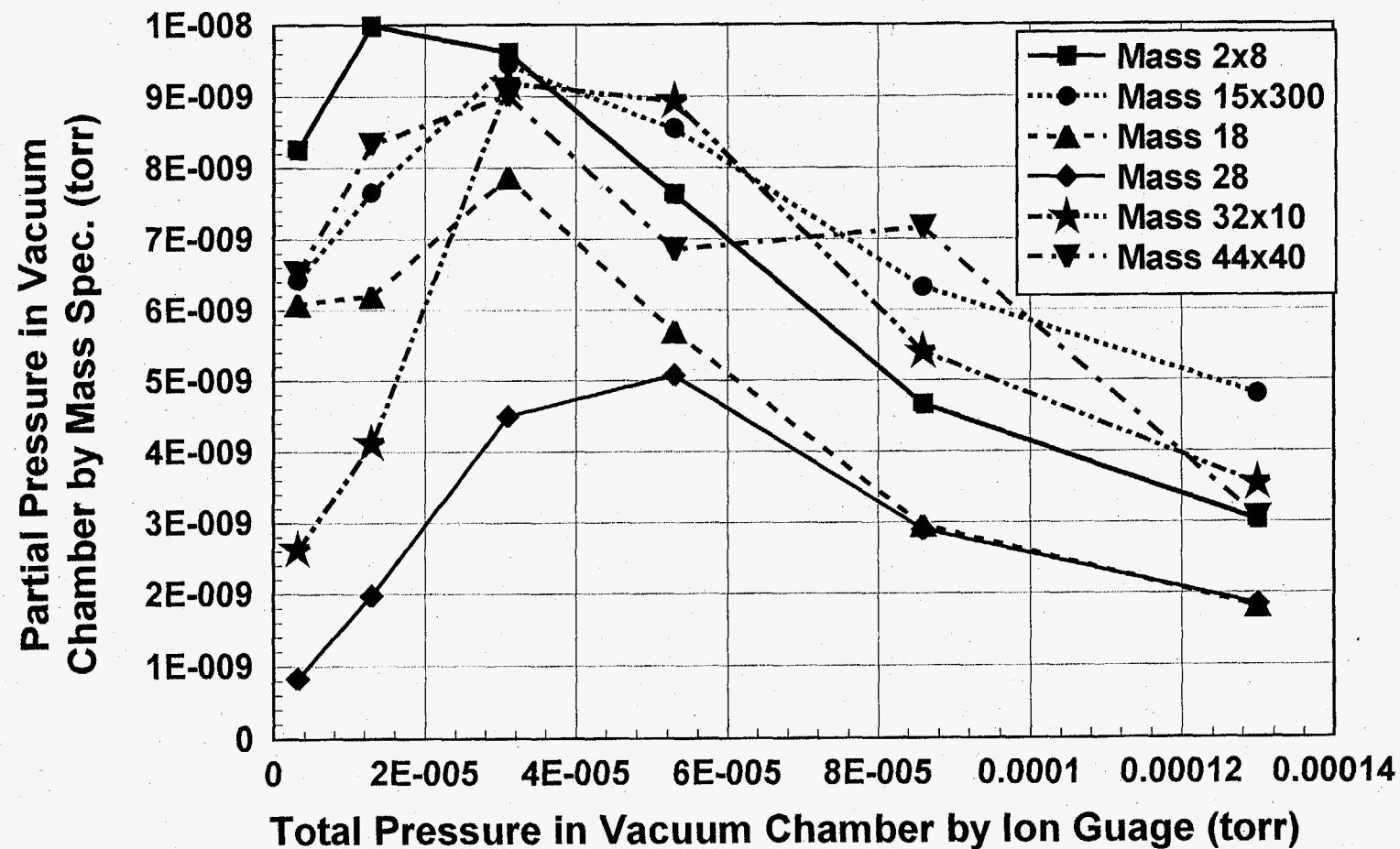


Figure 4: Background Partial Pressure of Various Masses as a Function of Vacuum Chamber Pressure, Purge Gas = AGA UHP Argon (99.999%)

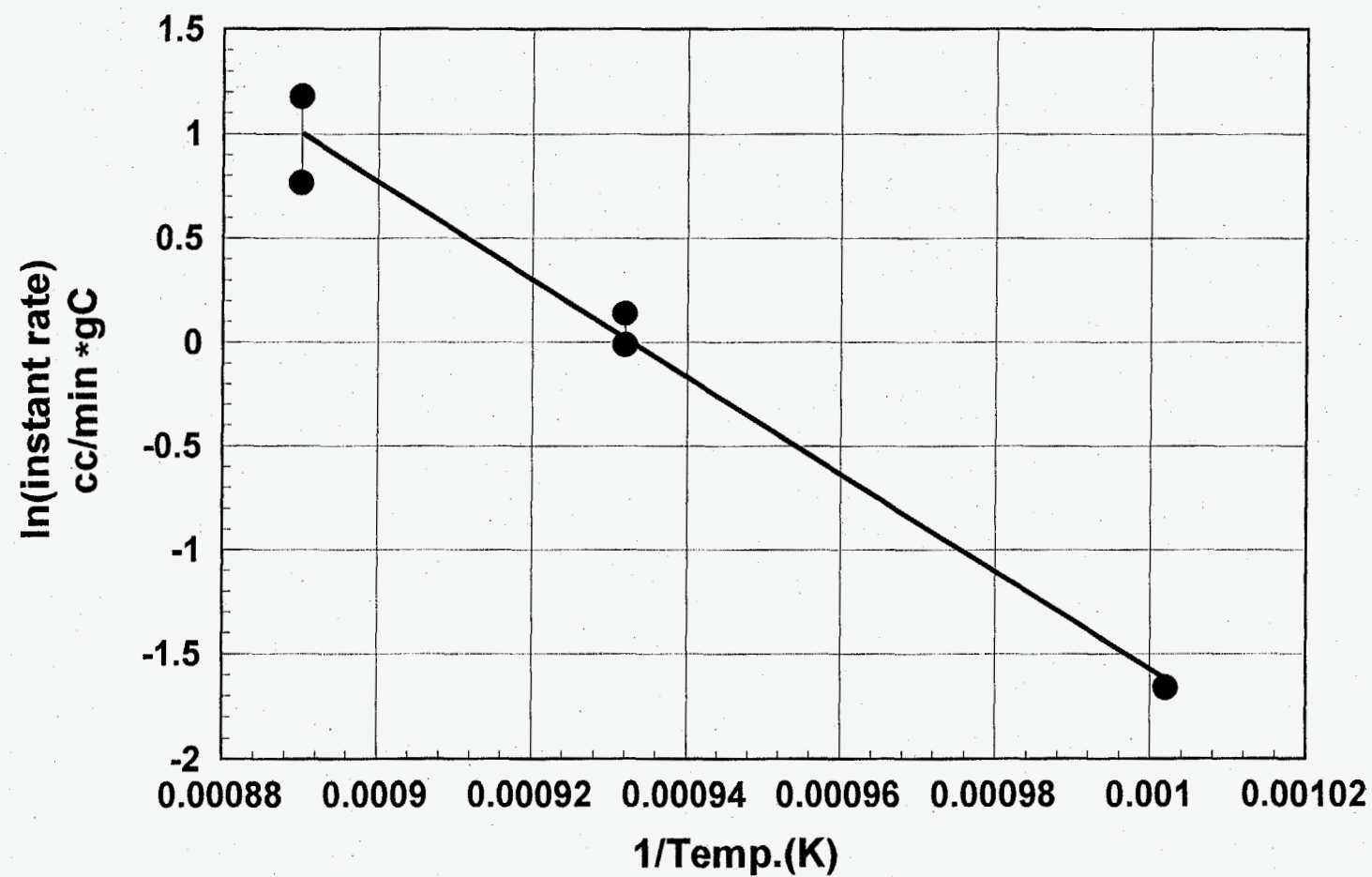


Figure 5: Arrhenius Plot for Steam Gasification of Annealed Saran Char:  $p_p(\text{steam}) = 200 \text{ psi}$



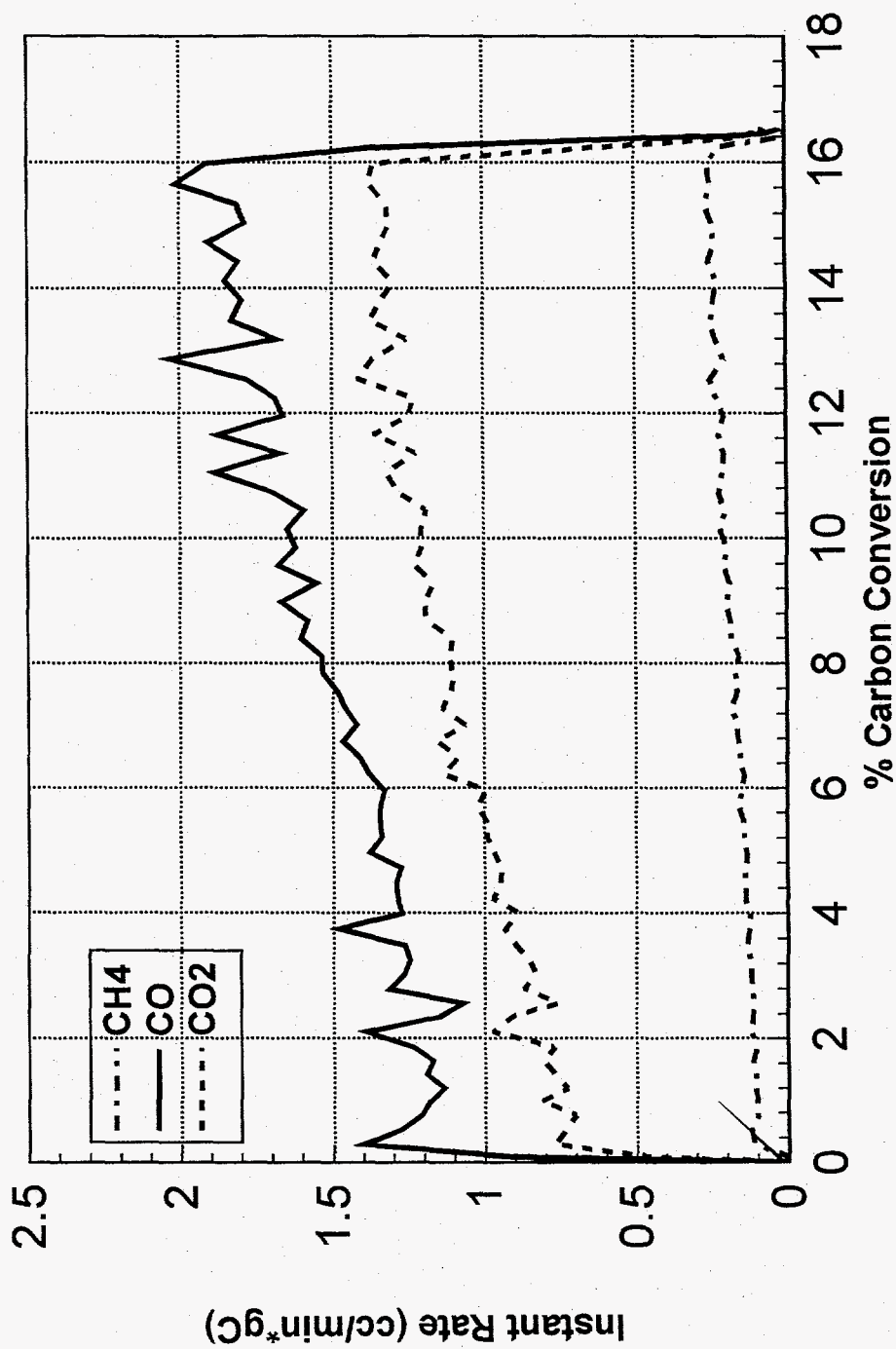


Figure 6: Annealed Saran Char Steam Gasification  
at 850°C and 200psi Steam Partial Pressure