

EVIDENCE FOR THE TRIBOCHEMICAL GENERATION OF HYDROGEN FROM HIGHER RANK COALS

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ABSTRACT:

Analysis of gases in sealed ampoules of higher rank Argonne Premium Coal Samples over a period of years has revealed the presence of significant (up to about 18%) constant amounts of hydrogen and increasing amounts of carbon dioxide. Comparison with the gas contents of sealed 55 gallon drums which have not been pulverized indicates that these gases came from activity following the collection of the samples. Several hypotheses are examined. The evidence indicates a possible tribochemical reaction involving fresh surface generated during pulverizing in the nitrogen atmosphere. It is probable that water reacts with the coal surface to release hydrogen. The oxygen from the water appears to bound to active sites, and later diffusion leads to formation and release of carbon dioxide.

INTRODUCTION:

The Argonne Premium Coal Sample Program (1) has produced a set of coal samples which have been sealed in glass for periods of up to 9 years. As part of a study of the stability of these samples, analyses of the gas in the ampoules have been made at varying intervals. The original objective of studying the oxygen concentration was readily met, and the analytical data provided additional insights into interesting changes during the storage period and also in the processing of the coal itself.

It has been observed (2) that a number of gases have accumulated. Not surprisingly, the lower rank coals release carbon dioxide and the higher rank coals evolve methane. It has also been observed that substantial amounts of hydrogen have been found in the samples of some of the higher rank coals. In addition increasing amounts of carbon dioxide were observed in some of the higher rank coals.

A number of hypotheses were formulated and tested to account for these observations. This paper describes the hypotheses and efforts to understand these observations.

EXPERIMENTAL

The collection of the Premium Coal Samples was done with very fresh samples which were transferred to 55 gallon stainless steel drums. These drums were taken to the surface of the underground mines, and purged with argon gas within .5-5 hours of the collection. Purging continued to give about 100 ppm or less of oxygen in the drums, with an overpressure of a few psi. After 1-2 days of travel to the Argonne National Laboratory, the drums were processed in a large (2000 ft³) glove box containing a crusher, pulverizer, mixer-blender and packaging equipment. This glove box was filled with nitrogen and kept at or below 100 ppm oxygen during the processing.

For a typical processing, the coal was initially crushed to pass between bars spaced at .5", pulverized to -20 mesh, and blended in a one ton batch. Half a ton of -20 mesh coal was packed in 5 gallon leverlock pails, moved through air locks and repulverized to -100 mesh. About 80% of the coal was placed in 5 gallon glass carboys, while the balance was sealed in ampoules containing either 5 grams of -100 mesh or 10 grams of -20 mesh material. The sealing was done with a torch using stoichiometric hydrogen and oxygen, controlled with a mass flow controller.

At all processing times, the gas contents in the glove box were monitored by an oxygen analyzer, hydrogen analyzer and total hydrocarbon analyzer (Beckman model 108A). Sample lines led from central points in the box, air locks, and other critical locations in the system to the analyzing system.

The oxygen concentration in the box was controlled during the operation by circulating the atmosphere through ductwork connecting the boxes to a catalytic reactor containing palladium-on-alumina catalyst. The reactor was connected to a supply of hydrogen which permitted the impurity oxygen to combine to produce steam. Upstream from the catalytic reactor were a high efficiency particulate filter with pressure differential measuring equipment and a cyclone separator for larger particulate material.

In operation the hydrogen concentration in the box was to be kept below 1.0%. The gauge had a single range with a maximum reading of 5%.

A typical sample consisted of one ton of coal held in six drums. A seventh drum was collected and retained for archival purposes. The gas pressure in the drums increased substantially for some samples and periodically required release of some gas for safety.

RESULTS AND DISCUSSION

Gas analyses were run by the Analytical Chemistry Laboratory at ANL and reported in volume percent. A set of ampules was provided which were opened in an evacuable chamber in a CEC mass spectrometer, and more recently in a VG 3001 mass spectrometer.

The data were reported for the species which were observed by the analyst. These species were: nitrogen, argon, water vapor, methane, carbon dioxide, ethane and higher hydrocarbons and hydrogen. The use of the VG spectrometer permitted resolution of the nitrogen and carbon monoxide in more recent measurements. Recently ammonia was also observed and other samples were checked for this gas.

In general the concentrations of a gas are higher in the -20 mesh ampules than the -100 mesh containers. The gas volume per gram of coal is comparable for most samples. The exception to this generalization is hydrogen. For hydrogen, the concentrations are higher in the -100 mesh ampules. This observation is consistent with a process-related origin for the majority of this gas.

The results obtained for the carbon dioxide analyses (six highest concentrations) are indicated in Figure 1.

The results for the hydrogen analyses are shown in Figure 2.

The operating records for the processing were checked for appearance of hydrogen in the process gas analysis system. In all cases with substantial release of hydrogen, the monitor indicated a rapid increase at the time the pulverizing started. The hydrogen supply to the catalytic reactor was checked, found to be normal, and shut off to prevent additional hydrogen entering the system from the gas cylinder.

Several hypotheses to explain the rapid appearance of the hydrogen and the slower appearance of the carbon dioxide were developed. Discussions with a number of individuals led to more. A summary of them follows, together with comments in support and against them.

Hypothesis 1: "The hydrogen and carbon dioxide were in the higher rank coal. The hydrogen was released more quickly because of its lower molecular weight."

Comments on hypothesis 1: The gases in the archival drums were sampled and analyzed. Hydrogen was below the limits of detection (.015%) while the hydrogen from the initial analysis of a -100 mesh Pocahontas ampule was 17.6%. Further, the carbon dioxide content of the gas in the drum of Pocahontas coal was 0.82%, while the methane was 52.9 and the ratio of the two was 0.016. The recent measurement of carbon dioxide in the -20 mesh sample gave 4.7% and the methane was 6.5% for a ratio of 0.72. Evidently much more carbon dioxide is evolved in the ampule than the drum.

Hypothesis 2: "The gases were produced by microbial action."

Comments on Hypothesis 2: Different workers have cultured samples. Some find no growth, while others find growth but only on low rank samples.

Hypothesis 3: "Coal dust found it way to the palladium catalyst, and lost hydrogen there."

Comments on hypothesis 3: The volume of the box is 2000 ft³. The hydrogen content from the Pocahontas sample was up to 14.7%. That represents almost one pound mole or about 2 pounds of hydrogen. Since the coal is about 4% hydrogen, the observed concentration would require the equivalent of about 40 pounds of coal accumulating on the catalyst bed and losing all of the hydrogen. Such a substantial deposition would require a major break in the filter and would have been observed in a notable drop in the pressure differential across the filter. That drop was not observed.

Hypothesis 4: "The methane gas coked on the palladium catalyst, releasing hydrogen". That may have been possible, however the catalyst activity did not decrease as might have been expected. The carbon dioxide generation is not explained by this hypothesis.

Hypothesis 5: "Low temperature oxidation produced the hydrogen as a byproduct."

Comments on hypothesis 5: Low temperature oxidation has been shown to produce hydrogen as a byproduct gas (5,6). The reported hydrogen gas concentrations range up to 1121 ppm for reaction with oxygen over 65 hours. The experiments showed about 11 ppm per 1% of oxygen consumed at 95°C. The hydrogen concentrations observed in the ampules from the processing facility ranged up to 17.6% (176,000 ppm) or two orders of magnitude greater than the maximum observed for the low temperature oxidation studies. The hydrogen production in the facility is a moderately rapid reaction during and after pulverizing. The oxygen consumption reported is much greater than the hydrogen production. In the processing facility the oxygen available was less than 100 ppm, while the hydrogen production was four orders of magnitude greater. The relative humidity in the processing facility was indicated to vary from 42 to 91%. A significant amount of moisture was available for reaction.

Hypothesis 6: "Tribochemical reactions are responsible for both of the gases."

Comments on hypothesis 6: Tribochemistry deals with the chemical reactions that are due to adding mechanical energy to a system (3). Pulverizing is an example. The surface of a solid is disturbed to a depth of about 10 atom layers in many solids during pulverizing. The disrupted zone is called the Beilby layer. The imperfections caused by grinding permit gases to readily diffuse through the damaged surface into the Beilby layer. During pulverizing fractures cleave bedding planes for the coal, but also break through the large macromolecular structure, rupturing carbon-carbon and other bonds. Radicals are created in this process. Water molecules are present from water contained in the coal and in the gas atmosphere. Through a succession of reactions, the water molecules could react with active sites on the fresh surface, and hydrogen could be removed while oxygen remained bound to the surface. The hydrogen could escape quickly, giving the rapid observed increase in hydrogen concentration. The slower increase of carbon dioxide could be attributed to a slow diffusion of oxygen around the surface until two oxygen atoms joined a removable carbon to form carbon dioxide.

CONCLUSIONS

The observation of an increasing hydrogen evolution with some higher rank coals during the processing of the large chunks into pulverized material has been made. Carbon dioxide has also been observed, but in smaller amounts. A number of hypotheses have been examined to explain this behavior. The most plausible at this time seems to be the tribochemical generation of hydrogen due to the creation of chemically active sites as a result of the

pulverizing. Reaction of moisture with the coal results in relatively rapid release of hydrogen and bonding of oxygen to the surface. A slow diffusion of oxygen around the surface coupled with release of gaseous carbon dioxide then follows. Additional work with isotope ratios for the carbon, hydrogen and oxygen species should help confirm the nature of the reactions and is planned.

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Fig. 1, Six Highest -20 Mesh Carbon Dioxide Concentrations

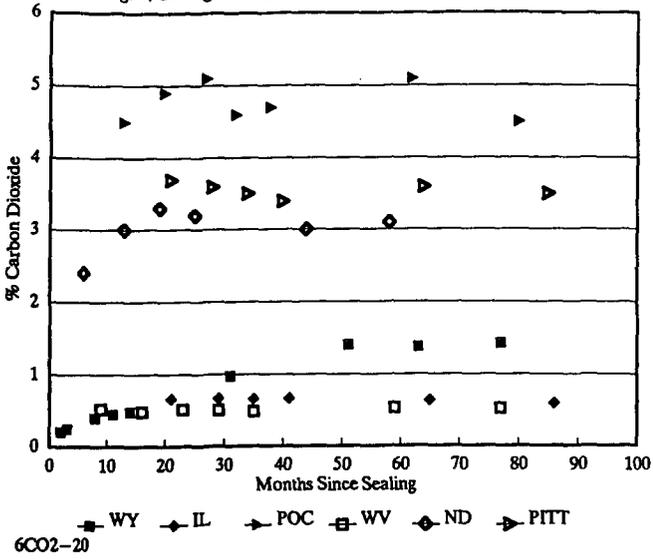


Fig. 2, Six Highest -100 Mesh Hydrogen Concentrations

