

AN APPARATUS FOR IN-SITU HIGH TEMPERATURE/HIGH PRESSURE ESR SPECTROSCOPY AND ITS APPLICATIONS IN COAL CONVERSION STUDIES

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Abstract

An apparatus for carrying out in-situ ESR (Electron Spin Resonance) spectroscopy studies from ambient to 500°C and for gaseous pressures up to 800 psi at x-band frequencies (~9 GHz) is described. ESR signals can be monitored as a function of time, temperature or pressure in the above stated ranges. Using this apparatus, results on the hydrogenation of a Blind Canyon coal carried out at 440°C in hydrogen pressures up to 600 psi, and with and without the shell 324 catalyst (presulfided NiMo/Al₂O₃), are described. A non-linear decrease of the free radical density with H₂ pressure is observed and the catalyst increases the free radical density. Significance of these results is discussed.

Introduction

The fundamental mechanisms of coal pyrolysis and direct hydroliquefaction are believed to involve free radicals and the interaction of the free radicals with available hydrogen.^(1,2) Generally accepted view of pyrolysis is that thermally generated free radicals extract internal hydrogen from coal to form tar or combine with other coal molecules to form high molecular weight char. In hydroliquefaction, when hydrogen is available readily from a donor solvent and/or molecular H₂, free radicals extract this hydrogen to produce low molecular weight product.^(1,2) In order to provide direct evidence for these views, direct and in-situ monitoring of the free radicals during pyrolysis and hydroliquefaction is necessary. In previous papers from this laboratory,⁽³⁻⁷⁾ we have used the in-situ ESR (electron spin resonance) spectroscopy of free radicals in coals to investigate pyrolysis and the effect of zinc halide catalysis in coal conversions. These studies were however carried out either in vacuum-sealed samples or in flowing gases (N₂ and H₂). Since direct hydroliquefaction is usually carried out under high pressures (1000-3000 psi) of hydrogen, it is essential to carry out ESR measurements under the realistic conditions of high temperatures/high pressures. Here we describe a microwave cavity system in which in-situ ESR spectroscopy can be carried out at temperatures up to 500°C and gaseous pressures up to 800 psi (pressures are limited by the use of the pyrex tubes). The design of our apparatus differs significantly from that reported by Petrakis and Grandy⁽²⁾ but somewhat similar to that described by Yokono et al.⁽⁸⁻¹⁰⁾ The major improvement in our apparatus is that pressure can be varied in-situ at a given temperature. Using this apparatus, we have investigated the hydrogenation of a Blind Canyon coal as a function of H₂ pressure at 440°C, with and without a catalyst. This apparatus, along with the results of these experiments, are described in this paper.

High Temperature/High Pressure ESR Cavity System

The high temperature/high pressure ESR cavity system consists of three primary units: (i) A rectangular TE_{102} cavity in which the field modulation coils are located outside the cavity and a circular hole through the center of the cavity which allows the insertion of the quartz dewar and the sample; (ii) A heating unit external to the cavity (see Fig. 1) and purchased from Wilmad Glass Co. in which a flowing N_2 gas over a voltage-controlled chromel heater is used to deliver heat to the sample without heating the microwave cavity; and (iii) a high pressure unit (Fig. 2) to which a pyrex ESR tube is attached which can be inserted in the TE_{102} cavity. If the sample is to be exposed to a flowing gas (such as N_2 or H_2), then the high pressure unit is replaced by the flow-chamber unit shown in Fig. 3, a description of which was also given in our recent paper.⁷ Thus in this apparatus, the cavity remains at ambient temperature and pressure and no cooling coils as for example used in the design by Yokono et al.⁽⁸⁻¹⁰⁾ are used anywhere in the apparatus. The system is pressurized directly from a gas cylinder and so the pressure can be easily changed during the course of the experiment. The maximum pressure is limited by the strength of the ESR tube and in our experiments, the pyrex and quartz tube could not withstand pressures beyond 800 psi. To attain higher pressures, search for a better non-conducting material for the ESR tube is underway.

There are several special features of the high pressure unit which deserve special mention. As shown in Fig. 2, the ESR tube is screwed to a stainless steel (#316) tube which in turn is connected to a high pressure gage and a valve to let in or shut off the gas supply. A Swagelok quick-connector connects this attachment to a stainless-steel bellow-type tube leading to the gas cylinder. To secure the sample tube firmly with the attachment, a stainless steel nut is glued to the tube using a high pressure glue (Torr-seal by Varian) and a stainless-steel block holds the tube below the nut giving additional support. The large temperature gradient between the bottom of the tube where the sample is kept and the top of the tube where the high pressure attachment is connected eliminated the need for any cooling of the tube. The high-temperature quartz dewar which is inserted in the hole of the TE_{102} cavity, has an evacuated double-wall ensuring only minimal heat transfer from the sample to the cavity. The gage connected to the tube enables direct reading of the inside pressure during experiment. Since inserting a thermocouple inside the cavity distorts the microwave signal, the thermocouple is placed outside, just at the cavity entrance. The temperature is calibrated by an initial run with an additional thermocouple inside the sample, the experiment being carried out under realistic identical conditions. In the heater unit, the temperature is controlled by the voltage input to the heater, controlled by a variable transformer. For each data point, at least 10 minute interval is allowed to ensure temperature stability.

Experimental Procedures

All experiments reported here were carried out with the Blind Canyon coal, DECS-17, obtained from the coal bank of the Pennsylvania State University. In Table 1, we list the proximate analysis, the ultimate analysis and the maceral content of this coal as provided by the coal bank. A presulfided catalyst, Shell #324 ($NiMo/Al_2O_3$) was obtained from the Consolidated Coal Co. An x-ray diffractogram of this catalyst is shown in Fig. 4. Not all the Al_2O_3 oxides lines are observed. From the two prominent lines observed near $2\theta \approx 46^\circ$ and $2\theta \approx 67^\circ$ and

using the Scherrer eq. $L = (0.9)\lambda/\beta \cos\theta$ (where L is the particle dimension, β is the corrected linewidth and λ is the x-ray wavelength) and the procedures outlined in our recent paper,⁽¹¹⁾ we find $L = 38 \text{ \AA}$ for the $2\theta \approx 38^\circ$ line and $L = 42 \text{ \AA}$ for the $2\theta \approx 67^\circ$ line. These measurements show that for the 324 catalyst, the average particle size $\approx 40 \text{ \AA}$. In our experiments, the 324 catalyst was dry mixed with the coal, in the ratio of 2.1% by weight of the coal.

The free radical density N is calculated by double integration of the derivative ESR spectra using an on-line computer and comparing it with a standard.⁽⁴⁾ Also the values of N are corrected for the Curie-law variation of the spins with temperature i.e. $N = N_T(T/RT)$, where N_T is the measured value at a temperature T in degrees Kelvin and RT is the room temperature in degrees Kelvin. If there is no change in the free radical concentration with temperature, then N will be independent of temperature and a plot of N vs T will be a horizontal line. To account for any changes in mass with temperature, thermogravimetric studies using the Mettler 3000 TG system were done. Typically 10 mg of the sample was heated in an alumina cell from 30°C to 600°C at a heating rate of $10^\circ\text{C}/\text{min.}$, in flowing N_2 and H_2 gases.

Results and Discussion

In Figs. 5 and 6, results of the thermogravimetric studies of the change in weight of the coal and the coal with catalyst, as a function of temperature and in flowing N_2 and H_2 gas, are shown. Two results are evident: more volatiles are lost in H_2 flow and second, the catalyst significantly reduces the evolution of volatiles in the presence of N_2 . These data were used to correct the free radical density N /mass for experiments carried out in N_2 and H_2 flow.

In Fig. 7, we have plotted N against temperature for the Blind Canyon coal under three conditions: (i) sample sealed under vacuum; (ii) experiments in flowing N_2 ; and (iii) experiments in flowing H_2 . For these cases, the variations of N with temperature are similar except above about 400°C , where N is lower in H_2 flow. This difference persists (shown in insert) even after applying the mass correction for N_2 and H_2 flow experiments. The lowering of N in H_2 flow is presumably due to capping of the free radicals by H_2 . Discussion of this variation of N with T , somewhat similar to the observation in other coals, is given in our earlier publications.^(3,4)

The effect of 2.1% loading of the coal with the 324 catalyst on N is shown in Fig. 8 where the experiments were carried out in flowing H_2 gas and the data are corrected for the change in mass from Figs. 5 and 6. These studies clearly show an additional mechanism for the generation of the free radicals by the catalyst. No additional details about this mechanism are, however, available at this time.

Since most of the experiments in direct coal liquefaction are carried out above 400°C and in H_2 pressures, we studied the variation of N as a function of pressure but at a fixed temperature of 440°C . A novel feature of our apparatus is that pressures can be varied in-situ. Results of N vs pressure are shown in Fig. 9, for the cases of coal and coal with catalyst in both H_2 and Ar gases. We used Ar gas suspecting that N_2 may have some effect on N . However later experiments showed that just as in Ar gas, there is no variation of N with N_2 pressure either. In H_2 pressure, however, there are significant changes in N with pressure as the

results in Fig. 9 show. For the coal alone, N decreases nearly linearly with P with initial pressures, approaching saturation above 400 psi. For the catalyst loaded coal sample, N increases slightly with initial pressures of H₂ but above 150 psi, N decreases nearly linearly with H₂ pressure. From these experiments, it is quite evident that molecular H₂ caps at least some of the free radicals whereas in the presence of the 324 catalyst, an additional mechanism for the generation of free radicals is operative.

There are only two reports available in literature on the variation of N with pressure in coals. Earlier studies by Petrakis and Grandy⁽²⁾ were done at two pressures viz. 1200 and 1600 psi of H₂ gas in the presence of tetralin. These studies showed no change in N with pressure, although the presence of tetralin which is an excellent hydrogen donor might have obscured the effect of H₂. On the other hand, it is possible, that as we observe in Fig. 9, the effect of H₂ is saturated above about 400 psi in the absence of a catalyst. Yokono et al⁽⁸⁻¹⁰⁾ measured N at 6 and 13 MPa of H₂ and N₂ (1 MPa \approx 145 psi) and found that H₂ aids in capping some of the free radicals. The results presented here in Fig. 9 are unique in that for the first time, a systematic study of N with H₂ pressure in the absence of tetralin is now available.

The results presented above have demonstrated that molecular H₂ is involved in free radical quenching reactions, supporting the hypothesis forwarded by Vernon.⁽¹²⁾ More recent studies on model compounds by McMillan et al⁽¹³⁾ and by Shin et al⁽¹⁴⁾ on the Argonn \grave{e} coals have shown that hydrogen can also take part in the hydrogenolysis of strong C_{ar}-C_{alk} bonds. Similar observations were made on hybrid studies in which known structures were either mixed with⁽¹⁵⁾ or grafted to coal.⁽¹⁶⁾ Although there is no direct proof of hydrogenolysis from our studies, the quenching of the thermally generated free radicals upon hydrogenation is quite evident. In addition, significant enhancement of the free radical density in the presence of 2.1% loading of the coals by the 324 catalyst provides strong evidence for catalytic cracking of coals. There is some evidence from the data in Fig. 9 that for initial H₂ pressure, this catalytic hydrogenolysis is more significant than the quenching mechanism for hydrogenation. Additional experiments in the presence of hydrogen donor solvents such as tetralin are now planned to further elucidate these mechanisms.

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Table 1: Relevant analysis of Blind canyon coal-DECS-17. Data obtained from Penn State Coal Bank.

proximate analyses (DAF %)		ultimate analysis (DAF %)		maceral content (DMMF vol%)	
volatile	50.04	C	81.61	inertinite	2.1
fixed C	44.93	H ₂	6.21	exinite	11.2
		N ₂	1.38	vitrinite	79.7
		total S	0.47	fusinite	6.0
		O ₂ (diff)	10.33		

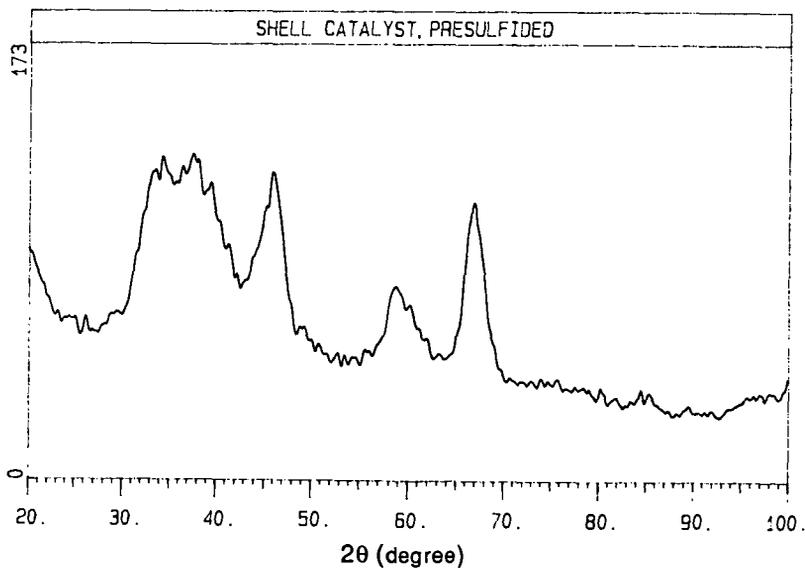


Figure 1: X-ray powder diffractogram of the catalyst, shell 324.

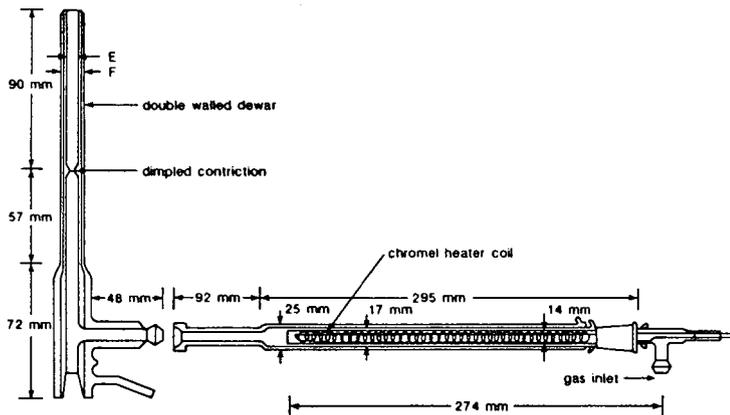


Figure 2: Block diagram of the high temperature dewar for ESR cavity

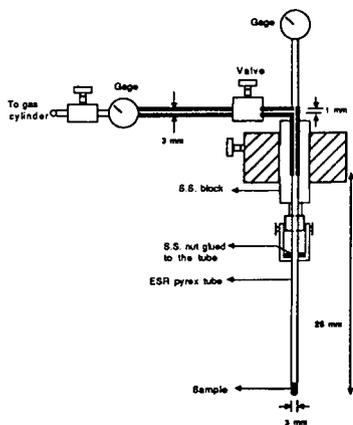


Figure 3 : Block Diagram of the high pressure set up fabricated for in-situ experiments up to 800 psi of any gas and up to 500 °C

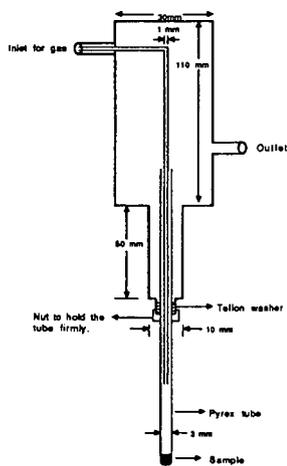


Figure 4 : Diagram of the flow chamber used for experiments under flowing gas.

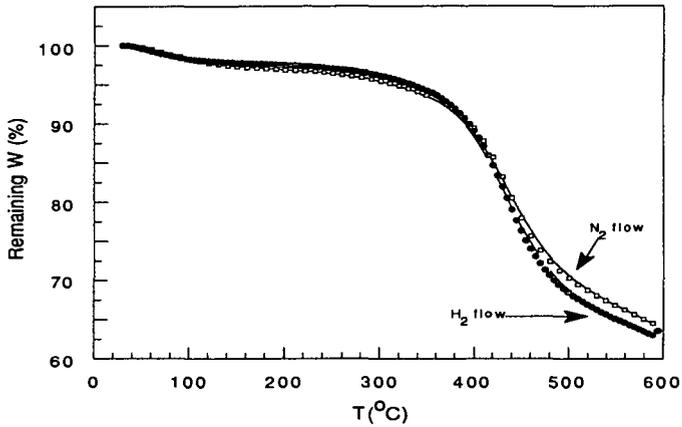


Figure 5: Remaining weight of blind canyon coal plotted against temperature, from TG experiments under nitrogen/hydrogen flow.

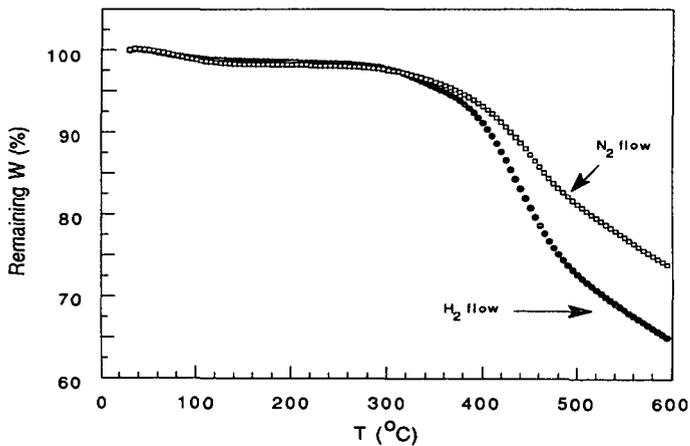


Figure 6: Variation of remaining weight with temperature for blind canyon coal mixed with 2.1% shell 324, under nitrogen/hydrogen flow.

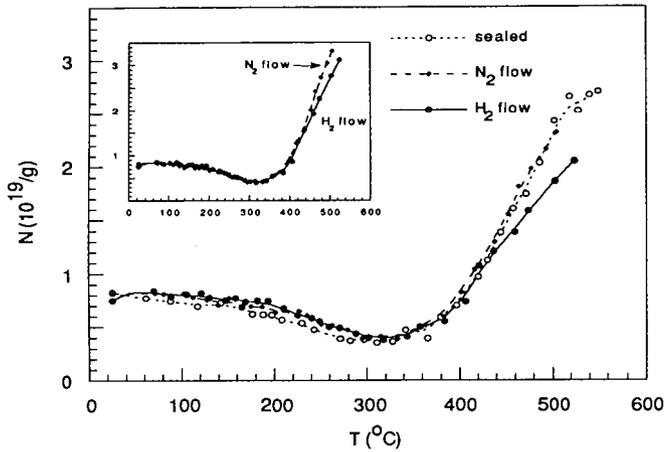


Figure 7: Variation of N with T for blind canyon coal. Plot after applying mass correction is shown in the insert.

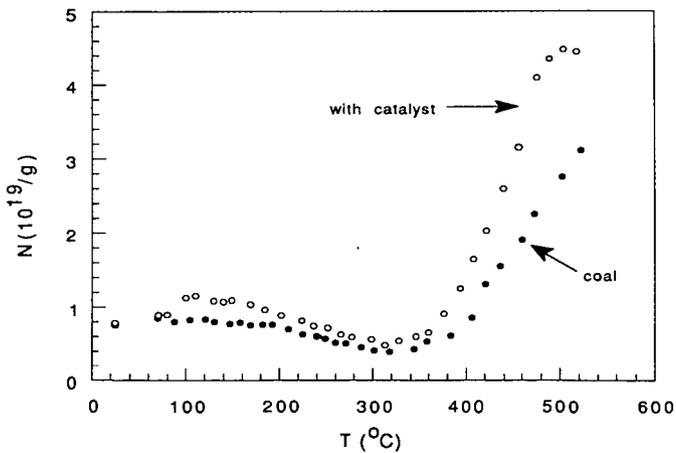


Figure 8: Variation of N with temperature for blind canyon with and without shell catalyst 324, in hydrogen flow. The values of N are corrected for the change in mass from TG data.

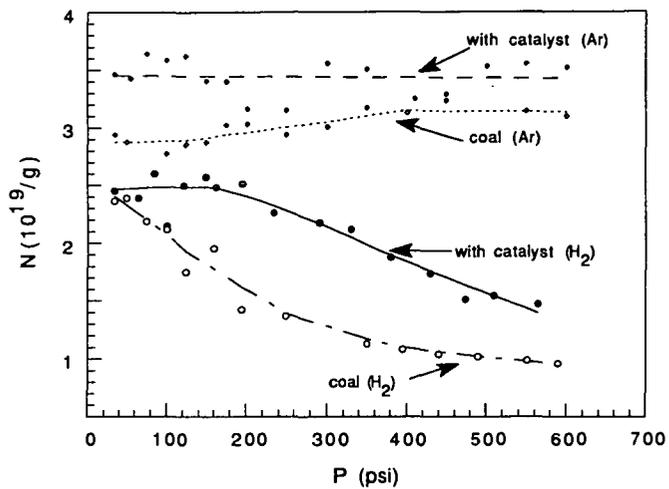


Figure 9: Variation of N with argon/hydrogen pressure for blind canyon coal with and without the shell catalyst 324.