

**TITLE:** Effect of Hydrogen Pressure on Free Radicals in Direct Coal Liquefaction/Coprocessing

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**OBJECTIVE:** To investigate the coprocessing of coal with waste tires and commingled plastics and to characterize the relevant catalysts, using high pressure/high temperature in-situ ESR (Electron Spin Resonance) spectroscopy. In this report, we will only concentrate on the recent results from high pressure ESR spectroscopy.

### **ACCOMPLISHMENTS & CONCLUSIONS:**

During this period, we made considerable progress in developing the high pressure capabilities in in-situ ESR spectroscopy and new results carried out in 1000 psi of  $H_2$  gas are presented in this report. In these experiments, we employ sapphire tubes to contain the high pressures at temperatures up to  $500^\circ C$ . Results of the experiments carried out under 1000 psi of  $H_2$  are compared with those under 1000 psi of non-interacting argon and with the earlier experiments in flowing  $H_2$  gas where the volatiles are removed by the flowing gas. In these experiments, the free radical density  $N$  of the Blind Canyon coal is measured at each temperature and pressure by double integration of the ESR signal and calibrating it against a standard. The details of our experimental apparatus and procedures have been described in earlier publications [1-3].

In Fig. 1, we show the temperature dependence of the free radical intensity  $N$  of Blind Canyon coal under three conditions: in  $H_2$  flow, in 1000 psi of argon (cold) and in 1000 psi of  $H_2$  (cold). In  $H_2$  flow experiments, the volatiles from the coal are swept away by the flowing gas and these volatiles from coal are known to contain ESR active free radicals [4]. The results in Fig. 1 show that in argon atmosphere,  $N$  is essentially temperature independent above  $200^\circ C$  suggesting that inert argon suppresses any thermolysis of coal. In 1000 psi of  $H_2$ ,  $N$  is significantly lowered at the lower temperatures as compared to the argon case suggesting significant hydrogenation (capping) of the free radicals. Above  $380^\circ C$ , we observe a dramatic increase in  $N$  due to cracking of coal in  $H_2$ . In flowing  $H_2$ ,  $N$  values are definitely lower than those compared to 1000 psi of  $H_2$ . As indicated above, this result may be due to the fact that the volatiles that are carried away by flowing  $H_2$  have free radicals [4], thus lowering the observed  $N$  in flowing  $H_2$ .

In Fig. 2, we show the effect of  $H_2$  pressure (up to 500 psi) at a fixed temperature on the free radical intensity  $N$ , both with and without a catalyst ( $NiMo/Al_2O_3$ ). For comparison, data from similar experiments carried out in argon gas is also included. The results from both Fig. 1 and Fig. 2 are consistent in that there is clear evidence that hydrogen pressure lowers the free radical intensity  $N$  by capping the free radicals. This is an important step in direct coal liquefaction since the free radicals formed during the thermal/catalytic decomposition of coal must be stabilized by transferring hydrogen from gaseous  $H_2$  and/or hydrogen donor solvent. The results presented in Fig. 1 and 2 show that this hydrogenation does indeed occur. In the presence of the catalyst ( $NiMo/Al_2O_3$ ), there is clear evidence of hydrogenolysis since the free radical intensity is enhanced as compared to the case of coal alone even though above about 150 psi of  $H_2$ , hydrogenation process takes over. These experiments clearly suggest that hydrogen in the presence of a catalyst promotes cracking of coal in addition to hydrogenation. Thus, in direct coal liquefaction, hydrogen plays the dual role of coal cracking and hydrogenation.

Next we consider the experimental ESR results of the coprocessing of coal with waste tire polymers. In Fig. 3, we show the free radical intensity  $N$  versus temperature for the Blind Canyon

coal, and for the coal mixed with Goodyear and Michelin tread in 1:1 ratio in flowing H<sub>2</sub> experiments. It should be noted that the tire treads by themselves do not yield any free radical ESR signal at the temperatures investigated in these experiments. Therefore the observed signals are from the coal alone, but including any catalytic effect of the tire polymers on the coal decomposition/hydrogenation. The results shown in Fig. 3 are interpreted as follows: First, the cracking temperature of coal which equals about 350°C in Fig. 3 is shifted downwards to about 240°C by the action of the tire polymers so that at the liquefaction temperatures (say 350°C-400°C), the free radical intensity of the coal is considerably enhanced by the action of the tire polymers; Second, although the magnitudes of N are different for the Michelin and Goodyear experiments, the observed effects are qualitatively similar for the two cases; and third, the drop in N above 400°C, may be either due to repolymerization of the free radicals or increased hydrogenation produced by the tire polymers.

Further insights into the role of tire polymers in coal coprocessing has emerged from the high pressure experiments with Michelin tire. These results are shown in Fig. 4, along with the data for H<sub>2</sub> from Fig. 3 and the results from experiment in 1000 psi of argon. Here we see a dramatic effect in 1000 psi of H<sub>2</sub> where experiment was repeated three times to confirm the findings. Departures of the data for 1000 psi of H<sub>2</sub> from the other experiments at temperatures around 160°C shows that 160°C may now be considered to be the cracking temperature of coal. Between 160° and 400°C, N continues to increase with temperature in 1000 psi of H<sub>2</sub> and increase in N for this temperature range is nearly three fold. It is indeed amazing that in 1000 psi of argon, N is severely suppressed as temperature increases. These experiments clearly show that in the presence of 1000 psi of H<sub>2</sub>, the tire polymers lower the cracking temperature of coal to about 160°C and promote significant decomposition of coal in the temperature range of 160° to 400°C. These results provide insight as to why tire polymers promote enhanced liquefaction [5]. In future experiments, we will be examining the combined effect of a donor solvent and molecular hydrogen in coal/waste tire coprocessing.

In conclusion, the results of in-situ ESR experiments up to 500°C and in H<sub>2</sub> pressures up to 1000 psi show that molecular H<sub>2</sub> caps the free radicals generated in the thermal decomposition of Blind Canyon coal. Furthermore, in the presence of the catalyst (NiMo/Al<sub>2</sub>O<sub>3</sub>) and tire polymers, additional bonds are broken at lower temperatures resulting in enhanced cracking of the coal. Thus, although it is generally accepted that coal liquefaction is a free radical process, our in-situ ESR experiments are providing the first clear evidence for the processes of hydrogenation, hydrogenolysis and catalytic cracking.

## PLANS:

In future experiments, we will be examining the effects of donor solvents in direct coal liquefaction/coal-waste tire coprocessing. Experiments are also underway for the investigations of the coprocessing of coal with commingled plastics. Results of these experiments will be reported elsewhere.

## REFERENCES:

1. M. M. Ibrahim and M. S. Seehra, Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem. 37, 1131-1140 (1992).
2. M. M. Ibrahim and M. S. Seehra, Energy Fuels 5, 74-78 (1991).
3. M. S. Seehra and B. Ghosh, J. Anal. Appl. Pyrolysis 13, 209-220 (1988).
4. S. S. Kim, M. L. Jarand, and K. Durai-Swamy, Fuel 61, 1124-1126 (1982).
5. M. Farcasiu and C. M. Smith, U.S. Patent 5,061,363, 1991.

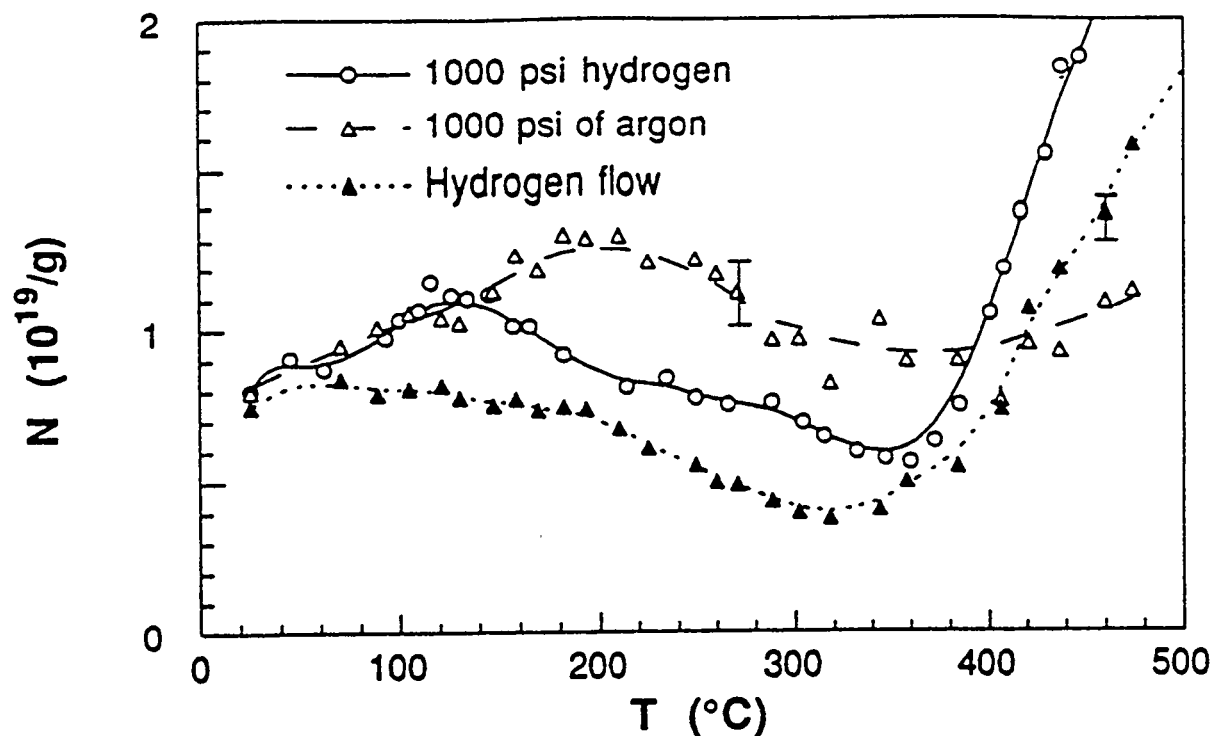


Fig. 1. Variation of  $N$  with temperature for coal alone in hydrogen flow and in 1000 psi of hydrogen/argon.

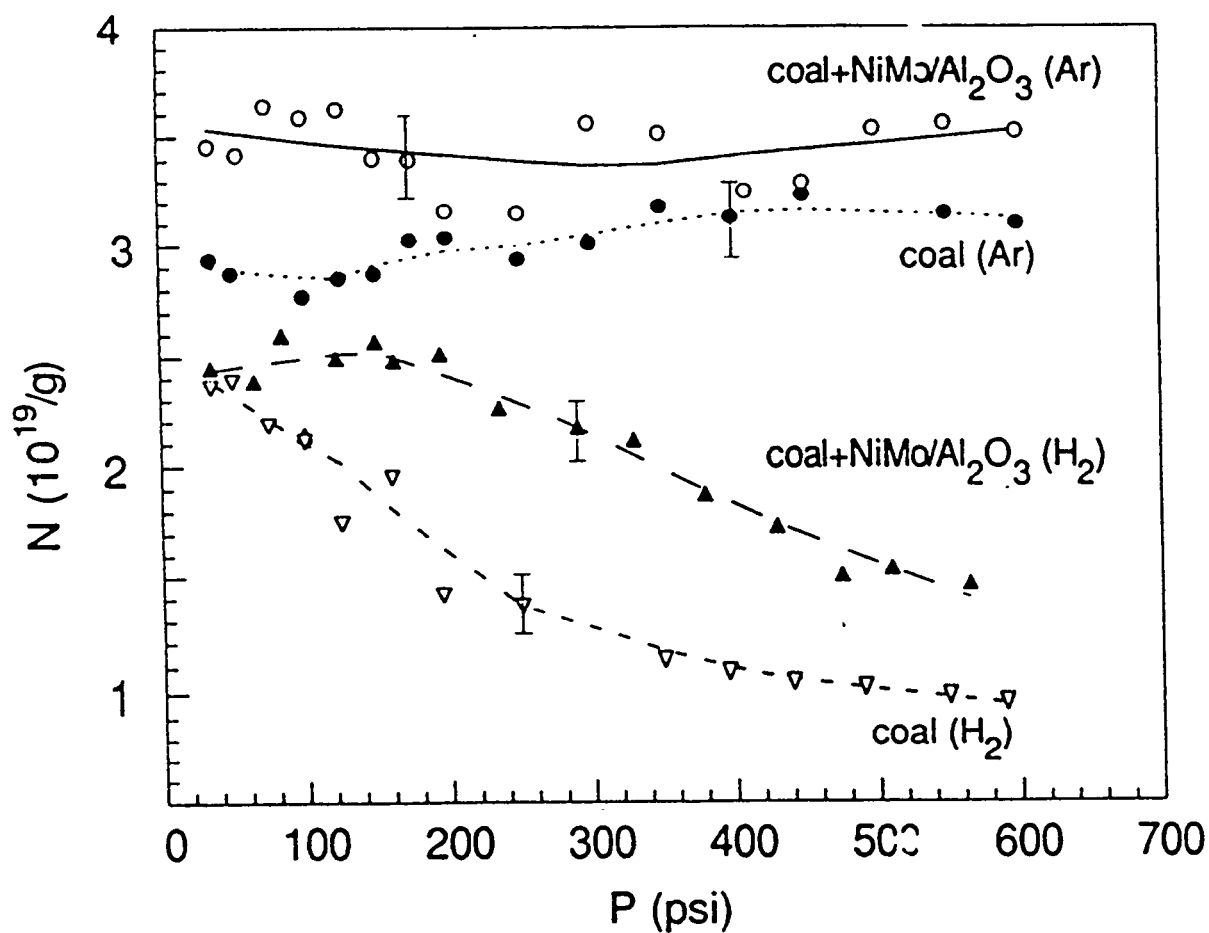


Fig. 2. Variation of the free radical intensity  $N$  with pressures of argon and  $H_2$  for Blind Canyon coal and the coal mixed with the  $NiMo/Al_2O_3$  catalyst (2.1% loading). The experiments were carried out at  $440^{\circ}C$ .

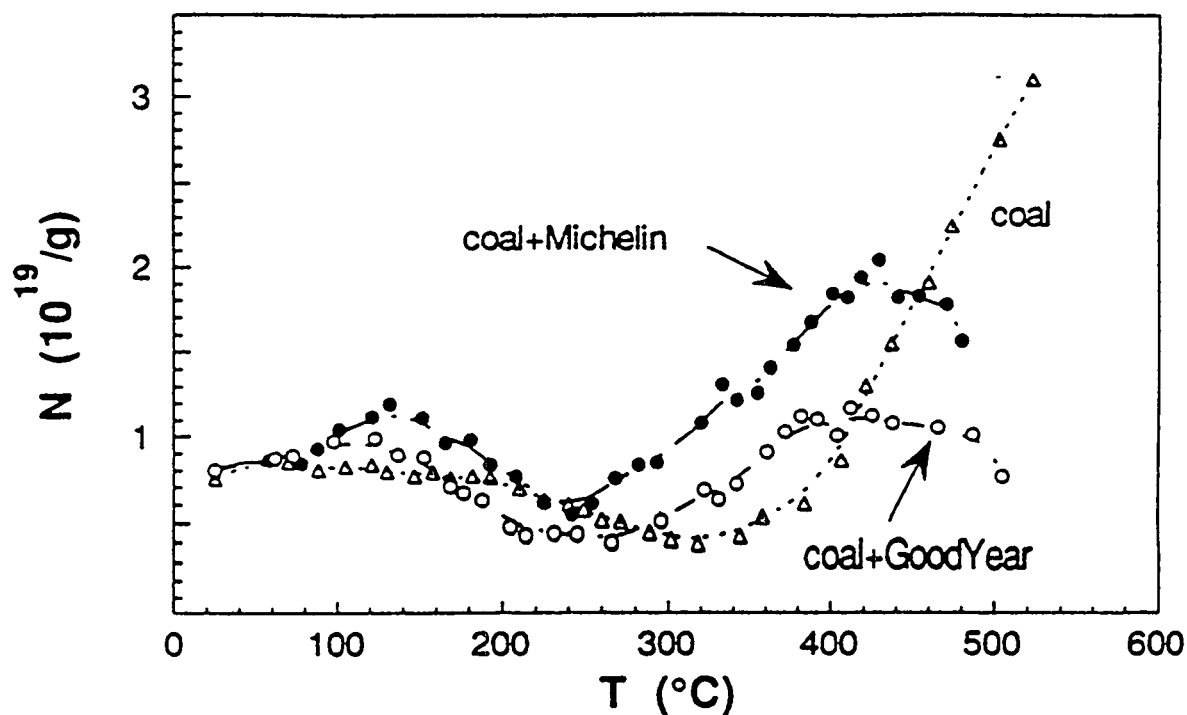


Fig. 3. Variation of  $N$  with temperature for coal and coal mixed with tread, for measurements in hydrogen flow.

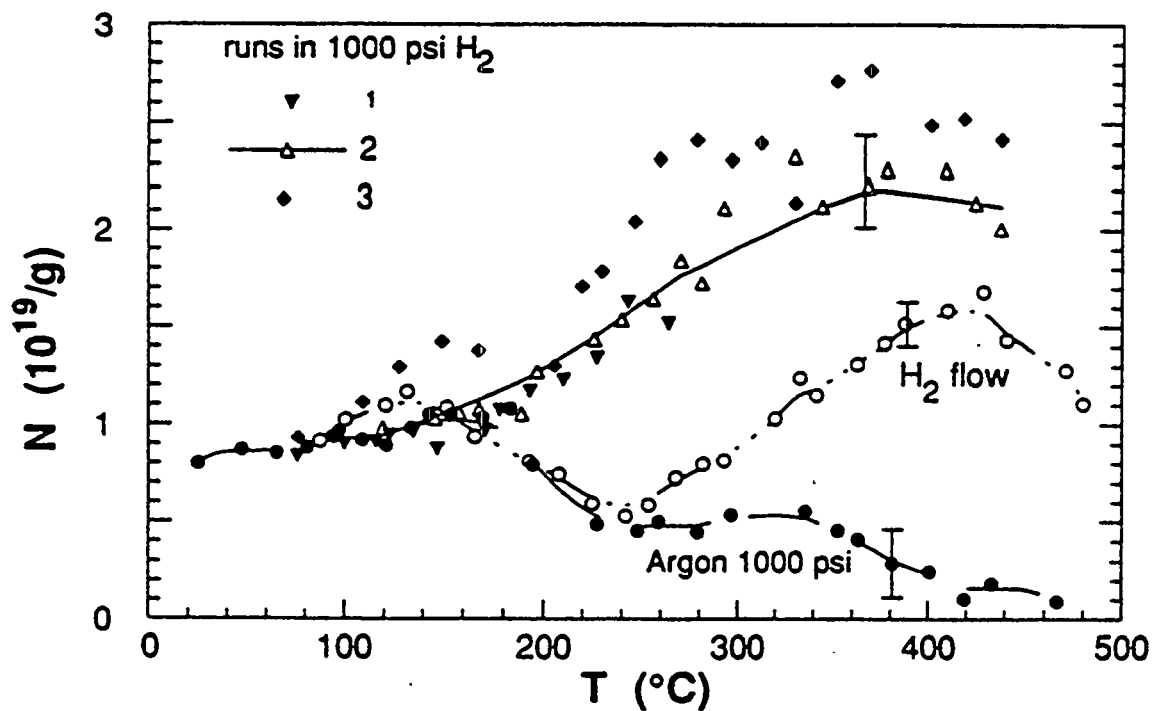


Fig. 4. Variation of  $N$  with temperature for coal + tread in hydrogen flow and in 1000 psi of hydrogen/argon.