

FORMATION AND BEHAVIOUR OF COAL FREE RADICALS IN RELATION TO LIQUEFACTION CONVERSION.

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ABSTRACT

The increase in radical concentration as measured by electron spin resonance (e.s.r) spectroscopy of four selected coals (Gardenne, Freyming, Mericourt and Escarpelles) was studied. The primary object of the study was to find, if any, the correlations between radical concentration and percentage conversion of these coals. Significant changes in radical concentration and in the chemical nature of the coals are observed as pyrolysis temperature is increased. The implications of free radicals in coal liquefaction are examined.

A gradual reduction in the number of free radicals over the temperature range (370 – 420⁰C) was observed in the liquid residue, Four hydroaromatic solvents (dihydrophenanthrene 1,2,3,4 – tetrahydroquinoline, tetralin and indan) were used to stabilize the radicals. The order of free radical stabilization in these solvents is Dihydrophenanthrene > Tetrahydroquinoline > Indan > Tetralin.

INTRODUCTION

Free radicals in coal and liquefaction products have been receiving increase attention hence the need to understand their role in coal conversion processes is very important [Benjamin et al 1978, Cui et al 2002]. Electron spin resonance (e.s.r) spectroscopy provides a convenient method of studying free radicals in coals, for it provides quantitative information as to their concentration and their nature [Benjamin et al 1978]

Coal liquefaction is basically a process of degradation and is normally carried out in the presence of a donor solvent and at high pressure in the process of coal pyrolysis various types of radicals are produced. If these radicals are not quenched or stabilized fast enough, for example, by H-donor solvents, the radicals will recombine to form polymers. Since the purpose of coal pyrolysis is to make light molecules by breaking bonds of larger molecules, the recombination reaction is highly undesirable [Cui et al 2002, Oviawe 1989, Oviawe and Nicole 2006a, Oviawe and Nicole 2006b]. In view of this, the effectiveness of the quench solvent in coal pyrolysis is a very important factor for the outcome of coal product liquids.

Free radicals are believed to play an important role in the mechanism of coal liquefaction [Oviawe and Nicole 2006b]. Numerous studies [Oviawe et al 1993, Patrakis and Grandy 1981, Ruxia et al 2004] have been carried out on the free radicals in coal using e.s.r. spectroscopy several authors [Srinivasan and Seehra 1982, Xu et al 2004] have studied the free radicals in coal liquefaction products. However, none of these studies made any attempt to correlate the concentration of the free radicals with the % conversion of the coal.

In this study, we report the results of room temperature e.s.r. measurements of some selected coal samples (Gardenne, Freyming, Mericourt and Escarpelles) that have been liquefied (to different degrees) in four hydroaromatic solvents (DHP, THQ, T and I) between 370 and 480⁰C under 12.4 Mpa of nitrogen. The reactivities of these coals and the relation between conversion and free radical concentration are discussed.

Experimental:

Four selected coals, Gardanne, Freyming, Mericourt and Escarpelles were dried

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in a nitrogen – swept oven at 105^oC for 2hrs. The hydroaromatic solvents: dihydrophenanthrene (DHP), 1,2,3,4 - tetrahydroquinoline (THQ), tetralin (T) and Indan (I) were purchased from Aldrich Chemical Co. and used without further purification. The hydroliquefaction experiments were carried out as previously described (Yokono et al 1986).

The coals used in the electron spin resonance (e.s.r) studies were ground to < 40 μm. The e.s.r measurements for both the liquids

and solid residues were taken at room temperature after heating at high temperature (370 – 480^oC). The analytical data for coal samples used in the experiments are shown in Table 1

In a previous study [Oviawe and Nicole 2006], the % conversion of each of the four coal samples was determined. The % conversion showed that Gardanne > Freyming > Mericourt > Escarpelles.

Table 1. Proximate and ultimate analyses of coal Samples:

	Gardenne	Freyming	Mericourt	Escarpelles
Volatile matter	45.2	37.6	23.4	9.3
Ash	6.7	5.5	29.9	12.3
Humidity	8.9	2.3	0.8	1.0
C	73.6	84.8	88.6	92.5
H	5.5	5.4	4.3	3.5
O	13.9	6.7	3.3	2.3
N	2.2	1.1	1.7	1.5
S	4.8	0.6	0.6	0.7

With this result we then decided to study the effects of temperature and nature of hydroaromatic solvents on the quenching of the thermally generated radicals in these coal samples.

Measurement of radical concentration at room temperature (25^oC)

The samples were prepared by placing ≈ 0.020g of coal mixed with ≈ 0.70g of silice (purity 99 %) in an e.s.r tube (quartz). The samples occupied a height of 2.2cm. For the liquid from the liquefied coal, 0.15cm³ (0.165g) was placed inside the esr tube, and it occupied a height of 2.2cm. The spectra were recorded at room temperature.

A solution of diphenylpicrylhydrazyl (DPPH) in benzene (1.106 X 10⁻³ mol / l) was prepared and used as the reference. An internal standard of powdered CuSO₄ · 5H₂O, sealed inside a capillary was used to regulate microwave field of the cavity.

The esr instrument used to measure the g-values, line widths and concentration of radicals in the coal samples was Varian v- 4500 spectrometer with dual cavity capacities. The details of the equipment and measurement procedures have been described previously [Benjamin et al 1978].

RESULTS AND DISCUSSION

The results showed that there is gradual reduction in the number of free radicals over the range of temperatures (370 – 420^oC) in the liquid

residue. On the other hand, a slight increase of free radicals is observed in the liquid pyrolysate. This shows that the hydroaromatic solvents are capable of quenching the free radicals produced from the breaking of weak linkages during the coal pyrolysis but are unable to stabilize the initial fossil radicals inherent in the coal samples.

At temperature above 440^oC, the reverse is the case for the radical concentration in the liquid pyrolysate and the coal pyrolysate. At this temperature, the thermal stabilities of these solvents become very important such that the solvents begin to degrade. The unstabilised radicals can then begin to attack the aromatic parts of the unliquefied coal molecule. The % conversion then decrease and the unstabilized free radical will then delocalize on the unliquefied coal pyrolysate.

This delocalization, added to the fact that at this temperature there are no more heteroatoms in the reduction of the values of line width (Fig 1) at half height (ΔH_{1/2}). Further more, at this temperature; the phenolic linkage begins to rupture.

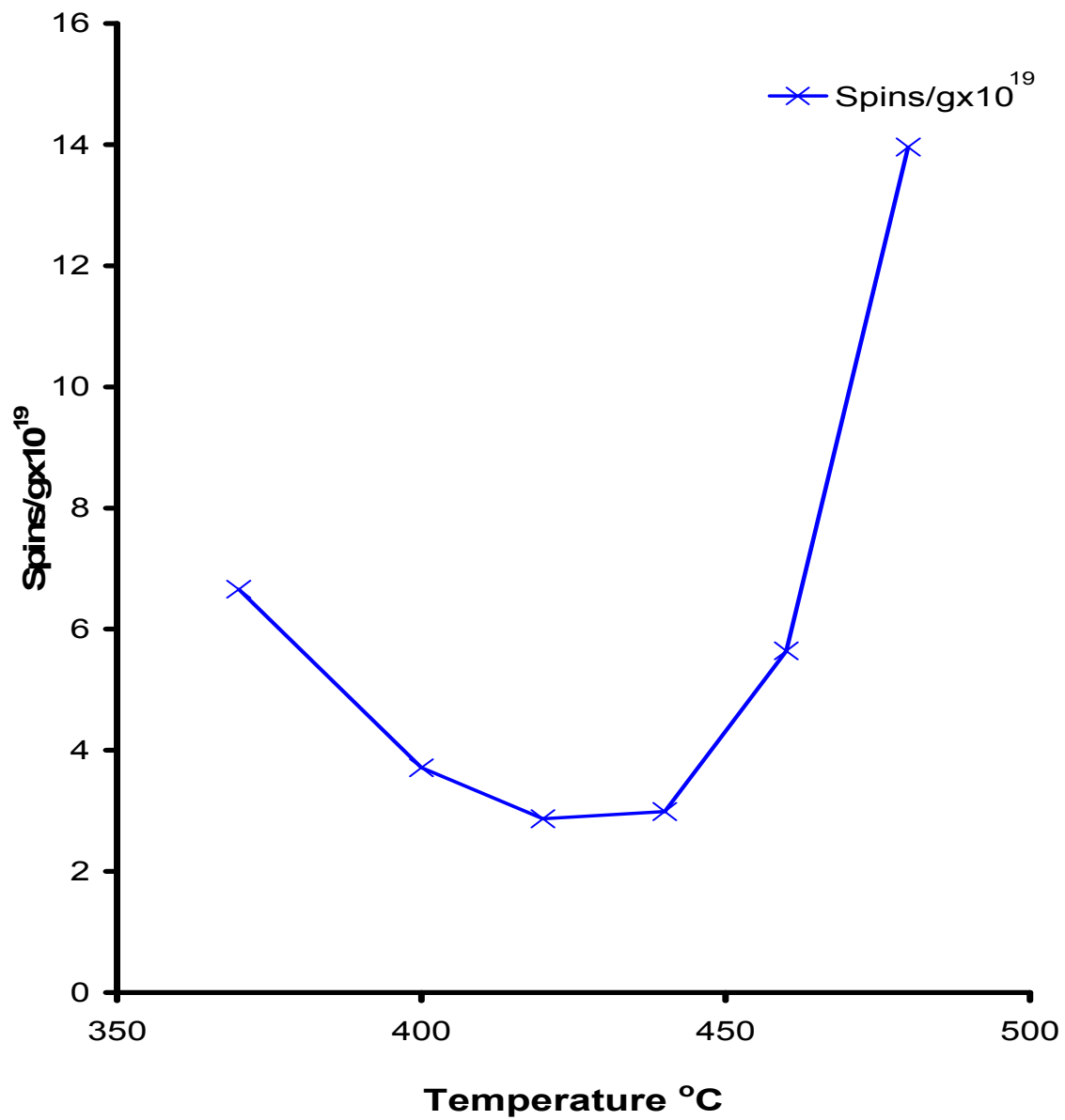
Experiments were performed separately using each of the four hydroaromatic solvents (tetralin, indan, 1,2,3,4 - tetrahydroquinoline and

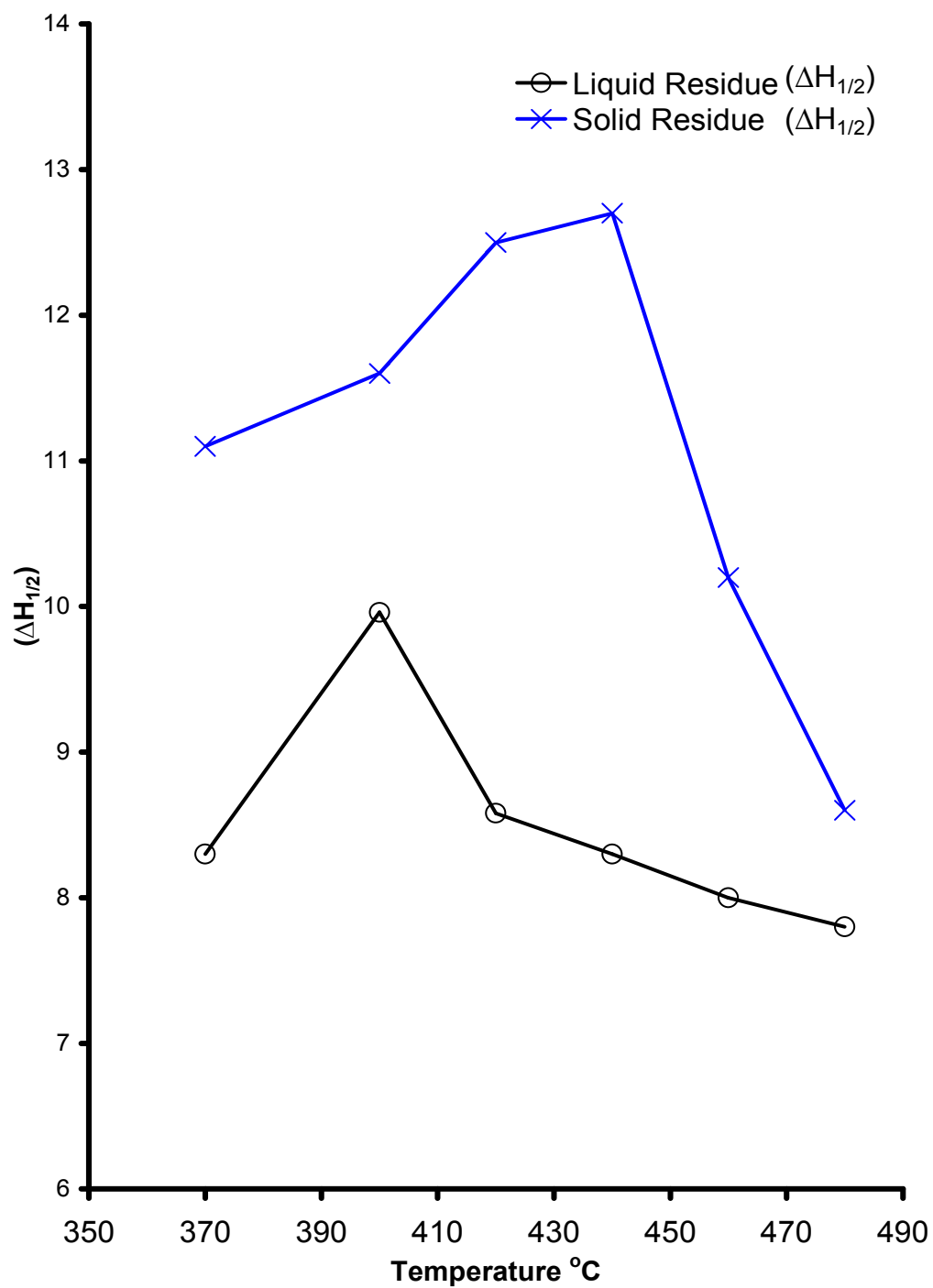
dihydrophenanthrene) to stabilize the free radicals issued from the pyrolysis of coal.

Due to the fact that abstraction of hydrogen from a hydroaromatic solvent lowers the number of free radicals within the reaction, an experiment performed using good hydrogen – donor solvent should result in a decrease of free radicals compared with the experiments performed with poor hydrogen - donor solvents. It is, therefore, logical to predict that the measurement of the concentration of free radicals in the pyrolysate should be correlated with good H-donor solvents for industrial uses. The spin concentration decrease with temperature (Fig 2) from 370 – 450°C. Above this temperature, a sharp increase in spin

concentration was observed. This is due to the fact that above 450°C, the solvent become thermally unstable.

The total concentrations of spins with each of the four hydroaromatic solvents were determined. As would be expected, DHP and THO were the most efficient solvents due to the fact that they easily transfer their donatable hydrogens to the radicals which are then stabilized resulting in the low concentration of spins observed in the experiments using these two H-donor solvents. The order of radical stabilization in these solvents is: Dihydrophenanthrene > Tetrahydroquinoline > Indan > Tetralin.





Line width at half height ($\Delta H_{1/2}$) at variable temperatures.

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