

ESR Investigations Related to Carbonization Tendency

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Introduction

Free radicals were first observed in coal as early as 1954 [1]. More recent investigations of coals, tar sands, bitumens, shales and petroleum feedstocks, as well as fractions of these source materials by ESR, indicate a significant number of 'native' free radicals [2]. In addition to these stable free radicals, additional radicals are produced on thermal treatment of these materials producing 'thermally-generated radicals' of various reactivities.

Previous work by several authors [3,4] has suggested a correlation between radical concentration and temperature for various coals. In this study a series of petroleum feedstocks was analyzed by ESR to determine if similar trends could be observed.

These ESR studies were performed at room temperature. The premise is made that the structure of the starting material is a function of how it will react at elevated temperatures. Though this may not be rigorously correct, the data obtained to date indicate that the general trend is followed.

Experimental

The samples used in the present investigation were vacuum residua and feeds to commercial coker units obtained from various refinery streams.

ESR spectra were obtained on a Varian Associates Model 4502-10A single cavity spectrometer employing 100 kHz modulation. CCR analyses were performed using ASTM D-189.

A DuPont Series 99 thermogravimetric analyzer (TGA) was used for all TGA char determinations. Elemental analyses were performed by Galbraith Laboratories.

Results and Discussion

The coking propensity as measured by CCR, TGA char and the free radical concentrations as determined by ESR are summarized in Table 1.

The results show that those feedstocks which possess a higher concentration of 'native' free radicals tend to form coke to a greater extent. The relation of CCR, and TGA char content to free radical concentration is shown in Figure 1. CCR is the accepted method of measuring coke formation; and TGA char has been applied and related to CCR [5].

It is postulated that the increase in radical concentration for the petroleum feedstocks is paralleled by an increase in the degree of polycyclic aromatic ring condensation. A highly-condensed ring system (low H/C ratio) is more closely related to the structure of coke and may therefore be related to the observed coking trend. In other words, if the components chemically resemble coke precursors then the transformation to coke is more direct and therefore more facile.

Recent data has confirmed that in a variety of petroleum derived heavy feedstocks as sulfur content increases,

Table 1. Coking Tendency as Measured by CCR and TGA Char and ESR.

Sample	CCR	TGA Char	[R·]/gram (x10 ¹⁷)
Zuluf Vacuum Resid	20.6	15.84	13.9
Joliet Coker Feed	14.38	9.30	3.33
Arab Light Vacuum Resid	10.77	7.20	1.12
Arab Light (650°F) Resid	—	5.75	0.92
Arab Light Resid	8.57	5.22	0.86
Slurry Oil	5.37	2.90	0.40

the free radical concentration measured at room temperature increases. This is shown in Figure 2.

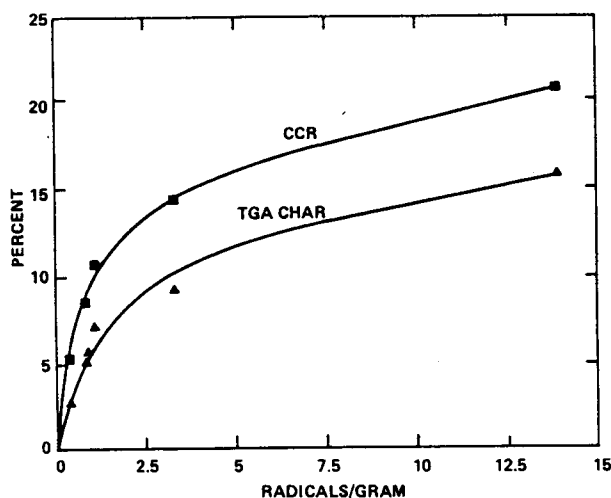


Figure 1. Radical concentration versus coking tendency.

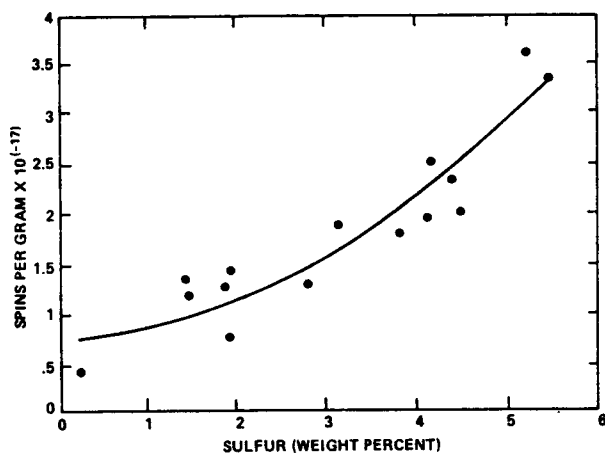


Figure 2. Spins concentration versus sulfur content

ESR Studies at Elevated Temperatures

TGA char studies as a function of spin concentration measured at 25°C for a series of residua showed that radical concentration increases with increasing TGA char.

These results imply that free radical concentration measured at 25°C is related to the tendency of a heavy petroleum sample to produce coke or carbon residue.

The question which arises is whether or not radical concentrations at elevated temperatures would produce a similar conclusion. Free radical concentrations for the same samples were measured at 350°C.

The relative free radical concentrations are approximately fifty times that of the 25°C values, however, the trends were similar.

Summary and Conclusions

The premise that the chemical structure of the starting feedstock determines at least in part the nature of the products after thermal treatment was confirmed for these samples. The structure and concentration of stable free radicals present in the feedstock are directly related to the composition of the sample. In addition, reactions produced at temperatures sufficiently high to cause bond rupture are a function of structure. Radical stability and, therefore, lifetime is also a function of structure.

Thus, if the component structures support stable free radicals at room temperature, then this may be reflected in the type of chemistry that will occur on heating the sample to relatively high temperatures, and therefore ESR may serve as a predictive tool. Further work at higher temperature is needed.

References

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