

CHANGES IN THE CHEMICAL COMPOSITION OF THE OIL FORMED WITH  
VARIATIONS IN HYDROGENATION CONDITIONS

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INTRODUCTION

There has been a number of studies of the chemical nature of coal hydrogenation liquids. However, the great majority of the coal hydrogenation liquids studied were produced using a liquid vehicle. The absence of a liquid vehicle may have an effect on the chemical reactions taking place and, therefore, on the chemical composition of the product obtained.

In the work reported here hydrogenation of coal was carried out in the absence of any vehicle oil in a semi-continuous reactor which allowed the volatile product to be swept from the reactor by a continuous stream of hydrogen. We here report our work on the changes found in the chemical composition of the oil (hexane soluble portion) with changes in hydrogenation reaction conditions. The hydrogenation conditions investigated were the catalyst (stannous chloride) concentration and the reaction temperature.

EXPERIMENTAL

Materials

The coal (0.50 to 0.25 mm fraction) used was from the New Wakefield Colliery, Transvaal. Analysis, air dried basis: Moisture 4.9; Ash 14.9; Volatile Matter 32.8%; dry ash-free basis: C, 79.2; H, 5.4; N, 2.1; S, 2.3%.

The catalyst was analytical grade stannous chloride. Stannous chloride was dissolved in water and added to the coal as an aqueous solution. The resultant slurry was mixed by stirring and then dried.

Hydrogenation

Hydrogenation was carried out in a reactor similar to the "hot-rod" reactor (1,2) designed by Hiteshue et al. The heating rate was ca 100°C/minute, and the time at temperature was 15 minutes. Hydrogen, at a flow rate of 22 l/minute, was continuously passed through a fixed bed of coal (25 g) impregnated with catalyst. The volatile products were condensed in a high-pressure cold trap. The other conditions are given in the Results and Discussion section.

The product was removed from the cooled reactor and from the condenser with the aid of toluene. The solid residue was extracted with boiling toluene (250 ml) in a soxhlet extractor for 12 hours. The toluene solutions were combined and the toluene removed under reduced pressure. Hexane (250 ml) was added to the extract and it was allowed to stand for 24 hours with occasional shaking. The solution was filtered to leave a residue (asphaltene) and the hexane was removed from the filtrate under reduced pressure to give the oil.

Fractionation of the oils

The oils were fractionated by adsorption chromatography on silica gel. The column was eluted successively with 40 - 60°C petroleum ether (12 fractions),

40 - 60 petroleum ether / toluene (increasing proportions of toluene, 5 fractions), toluene, chloroform and methanol.

### Analysis

I.r. and u.v. spectra were measured for each fraction from the columns. I.r. spectra were measured as smears on sodium chloride plates using a Perkin-Elmer 567 grating spectrophotometer, while u.v. spectra were measured as a solution in hexane (spectroscopic grade) using a Unicam SP 1700 instrument. Fluorescence spectra were recorded as described elsewhere (3).

$^1\text{H}$  n.m.r. spectra were recorded for the oils in deuteriochloroform at 90 MHz with tetramethylsilane as an internal standard using a Varian EM 390 instrument. Broad-band proton-decoupled pulse Fourier transform  $^{13}\text{C}$  n.m.r. were recorded in deuteriochloroform at 20 MHz using a Varian CFT-20 spectrometer.

Molecular weights were determined by vapour pressure osmometry in benzene solution using a Knauer apparatus. 5 concentrations over the range 1 - 5 g/l were employed and the molecular weight was obtained by extrapolation to infinite dilution.

The viscosities of the oils were measured using a Haake Rotovisco RV3 viscometer with a cone and plate sensor at 20°C.

### RESULTS AND DISCUSSION

From their i.r. and u.v. spectra, the fractions from column chromatography were grouped as saturate hydrocarbons, aromatic hydrocarbons and polar compounds. The last four fractions from the chromatographic separation were designated as polar compounds. All these fractions showed strong hydroxyl absorption in their i.r. spectra and these fractions contained acidic, basic and neutral compounds.

#### The effect of catalyst concentration

Four samples impregnated with 1, 5, 10 and 15% tin as stannous chloride were hydrogenated at 450°C and 25 MPa to investigate the effect that increasing catalyst concentration has on the composition of the oil (hexane soluble portion) formed.

Adsorption chromatography of the oils gave the percentage of saturate hydrocarbons, aromatic hydrocarbons and polar compounds in the oil. The percentage of polar compounds in the oil decreased as the catalyst concentration increased (see Figure 1) with mainly an increase in the percentage of aromatic hydrocarbons. The percentage of acids and bases in the oil were obtained by extraction with NaOH and HCl, respectively. There was a decrease in the percentage of acids and bases in the oil as the catalyst concentration increased (see Figure 1).

The i.r. spectra of the first fractions showed that they are aliphatic and contain no double bonds. In the C-H stretching region ( $\approx 3000\text{ cm}^{-1}$ ) the absorption due to methylene groups was much stronger than that due to methyl groups. Weak absorption in the region 720 - 735  $\text{cm}^{-1}$  was noticed in all the aliphatic fractions and is attributable to chains having four or more methylene groups (4). G.l.c. analysis of the saturate hydrocarbon fractions showed that the composition was similar to that reported for hydrogenation of a different South African coal (5). There were no noticeable changes with different catalyst concentrations.

The u.v. spectra of the first aromatic fractions of all the oils studied showed the presence of the naphthalenic structure. Strong absorption was seen at ca 224, 226, and 275 nm and weak absorption at 309, 318 and 323 nm. The shape and ratio of the absorbances were similar to those of a number of model naphthalenes recorded under identical conditions, and to the reported spectrum of naphthalene (6). The characteristic naphthalenic odour was also noticed in these fractions. Their i.r. spectra in the 3 000 cm<sup>-1</sup> region had strong aliphatic C-H absorption in relation to the aromatic C-H absorption. This may be ascribed to appreciable hydroaromatic and/or alkylaromatic structure.

The later aromatic fractions from the columns were analysed by u.v. and fluorescence spectroscopy. Though u.v. spectroscopy alone was of limited value in the characterization of these fractions, because of the incomplete separation, peaks and even inflections in the spectra were useful as guides for setting the fluorescence excitation wavelength. Full details of the method used, and of the fluorescence emission and excitation spectra of the polyaromatic ring systems identified have been reported elsewhere (3). Ten polyaromatic ring systems were identified by the similarity of their fluorescence excitation and fluorescence emission spectra to those of standard hydrocarbons. These were anthracene, 9,10-dialkylanthracene (model compound, 9,10-dimethylanthracene), pyrene, 1-alkylpyrene (model compound 1-methylpyrene), benzo(a)pyrene, dibenzo(def,mno)chrysene (anthanthrene), perylene, benzo(ghi)perylene, dibenzo(b,def)chrysene (3,4,8,9-dibenzopyrene) and coronene. All the polyaromatic ring systems were identified in all the oils analysed.

The i.r. spectra of the last four fractions of every sample studied showed strong OH absorption. The first of these fractions had sharp bands at ca 3530 and 3420 cm<sup>-1</sup>, whereas those of the subsequent fractions were broader and at lower frequency, presumably due to increasing hydrogen bonding (4). The aromatic C-H absorption was much weaker than the aliphatic C-H absorption, in the 3000 cm<sup>-1</sup> region. All the polar fractions have strong absorption in their u.v. spectra. Considerable absorption above 350 nm showed the aromatic nature of these fractions.

<sup>1</sup>H n.m.r. spectra were recorded for the oils produced at the various catalyst concentrations (1, 5, 10 and 15% Sn as SnCl<sub>2</sub>). The percentage of hydrogens in aromatic, benzylic and aliphatic environments showed no change with catalyst concentration.

<sup>13</sup>C n.m.r. spectra were also recorded for the oils produced. No discernible differences could be found between the spectra of the four oils. In the aromatic region, using the assignments of Bartle et al. (7), it was noticeable that the aromatic C-H (118 to 129 ppm from TMS) signals were much stronger than those due to aromatic C-C (129 to 148 ppm from TMS). Part of the aromatic C-H band was shifted to higher field (108 - 118 ppm) and may be attributed to aromatic C-H ortho to ether C-O (7). The aliphatic carbon bands extend from 12 to 50 ppm. Superimposed on the aliphatic carbon bands are sharp lines at 14, 23, 32, 29 and 29.5 ppm. These lines have been ascribed by Pugmire et al. (8) to the α, β, γ, δ and ε-carbons of long aliphatic chains. The intensity of the ε-carbon band is approximately four times the intensity of the α or β carbon indicating reasonably long aliphatic chains.

It was obvious on visual examination of the oils that the greater the catalyst concentration used, the less viscous was the oil produced. The decrease in viscosity with catalyst concentration is shown in Figure 2.

It has been reported that the molecular weight of coal liquids affects the viscosity (9,10). However, the decrease in molecular weight that occurred with increasing catalyst concentration was relatively small. (The molecular weights of the oils were 247, 241, 237 and 231 for 1, 5, 10 and 15% catalyst, respectively). We feel that this relatively small change in molecular weight would not cause such a noticeable change in viscosity unless changes in the chemical nature of the oil also contributed to the viscosity reduction.

Sternberg et al. (9) showed that the presence of asphaltenes in coal-derived oils caused a marked increase in the viscosity. This group also showed that these asphaltenes were acid-base complexes and that hydrogen bonding occurs between the acidic and basic components of asphaltenes (11,12). Recent work (10,13) on coal liquefaction bottoms has shown the importance of hydrogen bonding on the viscosity of coal liquids.

The reduction of polar compounds in the oil with increasing catalyst concentration could reduce hydrogen bonding and, therefore, the viscosity of the oil. To further look at this possibility, i.r. spectra were recorded at the same concentration in CCl<sub>4</sub> for each of the oils (see Figure 3). The i.r. spectra showed sharp peaks at 3610 cm<sup>-1</sup> (free OH), 3550 cm<sup>-1</sup> (2nd free OH?) and 3480 cm<sup>-1</sup> (N-H) and a broad peak at ca 3380 cm<sup>-1</sup> which is assigned to hydrogen bonded OH. This band decreases with increasing catalyst concentration (see Figure 3) indicating that hydrogen bonding in the oil decreases with increasing catalyst concentration used to produce the oil. The band at ca 3380 cm<sup>-1</sup> was shown to be due to intermolecular hydrogen (4, 14) bonding by recording the spectrum of a more dilute solution (using a longer path length cell), the 3380 cm<sup>-1</sup> band diminished with an increase in the 3610 cm<sup>-1</sup> peak.

It would appear that increasing the amount of stannous chloride catalyst, under our experimental conditions, as well as increasing the amount of oil formed decreases the amount of polar compounds in the oil which decreases the hydrogen bonding and therefore helps to decrease the viscosity of the oil. N.m.r. spectroscopy and evidence from the chromatographic fractions indicates that there is little change in the nature of the hydrocarbon fractions.

#### The effect of temperature

For this study, the pressure was 25 MPa and tin (1% of the coal) as stannous chloride was used as the catalyst. Some additional runs were also carried out at 15 MPa pressure. The temperature range studied was from 400°C to 650°C.

<sup>1</sup>H n.m.r. spectra of the oils were recorded for the range of temperatures and the protons were assigned as aromatic, phenolic OH, benzylic and aliphatic. There was an increase in the percentage of aromatic protons and a decrease in the percentage of aliphatic protons as the temperature increases, while the percentage of benzylic protons remained constant (see Figure 4). It, therefore, appears that as the hydrogenation temperature increases side groups are lost and that the C-C bond directly attached to the aromatic ring is more stable than those further from the ring. The molecular weight of the oil decreases with temperature (see Figure 5) as would be expected if side chains are being removed.

<sup>13</sup>C n.m.r. spectra were recorded for the oils produced at 400°C, 450°C, 550°C and 600°C. As the temperature increased the aromatic carbon bands became much more intense compared to the aliphatic carbon bands (see Figure 6). Quantitative estimation of the peak areas was not attempted due to the effect of variations in spin-lattice relaxation times and nuclear Overhauser enhancement with different carbon atoms. Superimposed on the aliphatic carbon bands were sharp lines

at 14, 23, 32, 29 and 29.5 ppm, which are due to the  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\epsilon$ -carbons of long aliphatic chains (8). As the temperature increases, these lines become smaller compared to the other aliphatic bands and this is especially noticeable in the spectrum of the 600°C oil. The  $\epsilon$  line was approximately four times the intensity of the  $\alpha$  and  $\beta$  lines at 400°C and 450°C, at 550°C approximately three times and at 600°C only about twice the intensity. It would seem that as the temperature increases, the long aliphatic chains are reduced in both number and length. (G.l.c. analysis of the saturate fractions from column chromatographic separation showed that as the hydrogenation temperature increases there was a decrease in the percentage of the higher alkanes and an increase in the percentage of their shorter chained analogues in the saturate hydrocarbon fractions). It was also noticeable when comparing the spectrum of the 600°C oil to the spectra of the 400°C and 450°C oils that the intensity of bands due to  $\text{CH}_3$ ,  $\alpha$  to aromatic rings (19 - 23 ppm from TMS (7)) had increased in intensity compared to the other aliphatic bands. This agrees with the  $^1\text{H}$  n.m.r. results which showed no change in the percentage of benzylic protons while the percentage of aliphatic protons decreased.

Elution chromatography gave the percentage of aliphatic hydrocarbons, aromatic hydrocarbons and polar compounds in the oil. There was a reduction in the percentage of polar compounds in the oil (see Figure 7) with subsequent increase in the aromatic percentage.

U.v. and fluorescence spectroscopy of the aromatic fractions showed the presence of the same aromatic structures as found in the oils from the catalyst experiments. The i.r. spectra in the 3000  $\text{cm}^{-1}$  region of the aromatic fractions varied with temperature. At low temperature the aliphatic C-H absorption was much stronger than the aromatic C-H absorption whereas at high temperature this difference was not so pronounced, which may be ascribed to a decrease in alkyl substitution as was shown by n.m.r. spectroscopy.

The viscosity of the oil decreases considerably with temperature as shown in Figure 8. The viscosity at the lower pressure 15 MPa was 90 mPa.s at 400°C and 9 mPa.s at 650°C. The decrease in viscosity is expected as there was a decrease in molecular weight with increasing temperature and also a decrease in the percentage of polar compounds in the oil.

The effect of increasing the hydrogenation temperature, under the conditions used here, is to give a more aromatic product of lower molecular weight containing fewer long aliphatic chains. The viscosity of the oil and the percentage of polar compounds in the oil also decrease with increasing temperature.

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#### REFERENCES

1. R.W. Hiteshue, R.B. Anderson and M.D. Schlessinger, *Ind. Eng. Chem.*, **49**, 2008 (1957).
2. J.A. Gray, P.J. Donatelli and P.M. Yavorsky, *Preprints, Amer. Chem. Soc., Div. of Fuel Chem.*, **20**(4), 103 (1975).
3. J.R. Kershaw, *Fuel*, **57**, 299 (1978).

4. L.J. Bellamy, "The Infrared Spectra of Complex Molecules", 3rd edn., Chapman and Hall, London, 1975.
5. J.R. Kershaw, S. Afr. J. Chem., 30, 205 (1977).
6. E. Clar, "Polycyclic Hydrocarbons", Vol. 1, Academic Press, London, 1964, p.212.
7. K.D. Bartle, T.G. Martin and D.F. Williams, Chem. Ind., 313 (1975).
8. R.J. Pugmire, D.M. Grant, K.W. Zilm, L.L. Anderson, A.G. Oblad and R.E. Wood, Fuel, 56, 295 (1977).
9. H.W. Sternberg, R. Raymond and F.K. Schweighardt, Preprints, Amer. Chem. Soc., Div. of Petrol. Chem., Chicago Meeting, August 24 - 29, 1975.
10. J.E. Schiller, B.W. Farnum and E.A. Sondreal, Amer. Chem. Soc., Div. of Fuel Chem., 22 (6), 33 (1977).
11. H.W. Sternberg, R. Raymond and F. Schweighardt, Science, 188, 49 (1975).
12. F.K. Schweighardt, R.A. Friedel and H.L. Retcofsky, Appl. Spectrosc., 30, 291 (1976).
13. K.A. Gould, M.L. Gorbaty and J.D. Miller, Fuel, 57, 510 (1978).
14. F.K. Brown, S. Friedman, L.E. Makovsky and F.K. Schweighardt, Appl. Spectrosc., 31, 241 (1977).

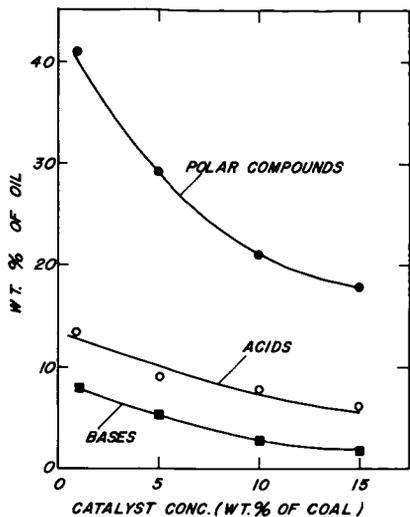


FIGURE 1 VARIATION OF POLAR COMPOUNDS, ACIDS AND BASES IN OIL WITH CATALYST CONCENTRATION.

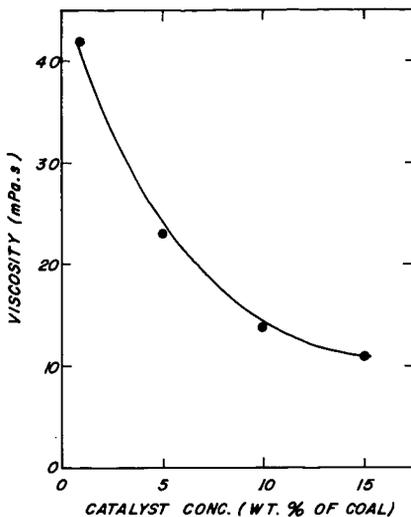


FIGURE 2 VARIATION IN VISCOSITY OF OIL WITH CATALYST CONCENTRATION

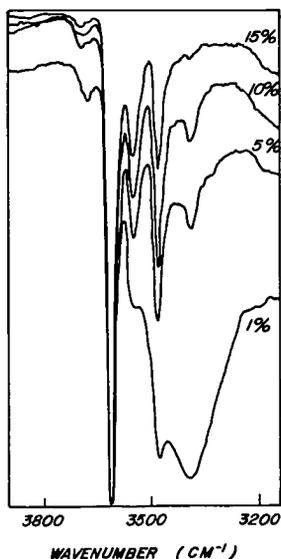


FIGURE 3 PARTIAL INFRARED SPECTRA OF OILS (VARIOUS CATALYST CONCENTRATIONS)

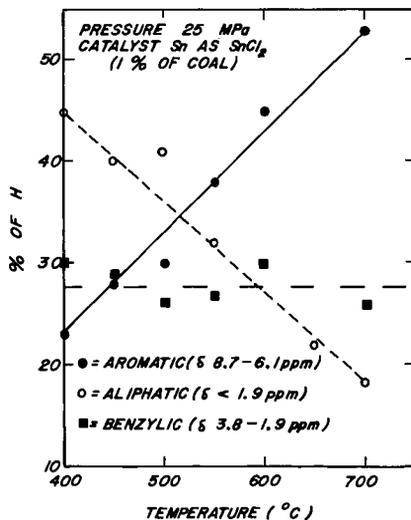
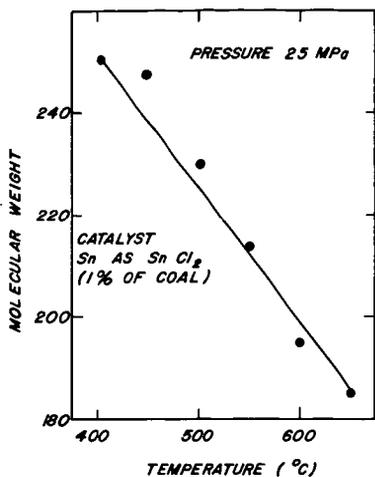
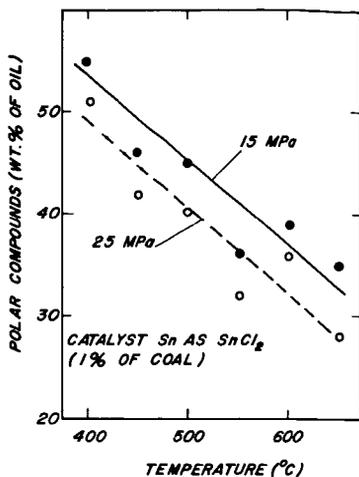


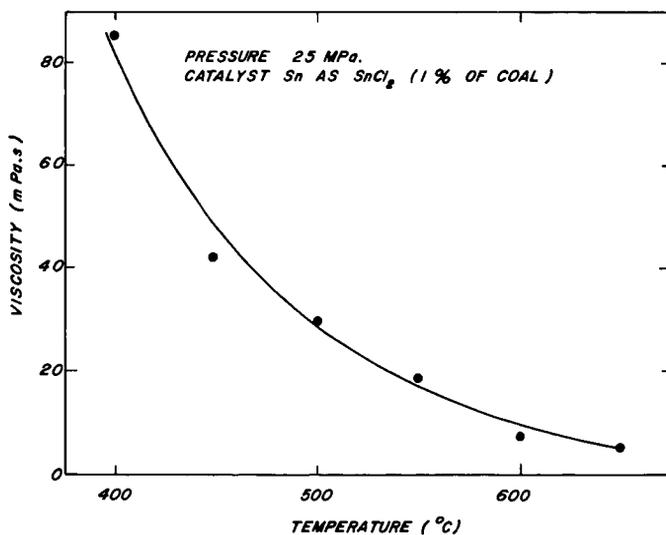
FIGURE 4 VARIATION OF HYDROGEN DISTRIBUTION WITH TEMPERATURE.



**FIGURE 5** VARIATION OF MOLECULAR WEIGHT OF OIL WITH REACTOR TEMPERATURE.



**FIGURE 7** VARIATION IN PERCENTAGE OF POLAR COMPOUNDS IN OIL WITH REACTOR TEMPERATURE.



**FIGURE 8** VARIATION OF VISCOSITY WITH REACTOR TEMPERATURE.

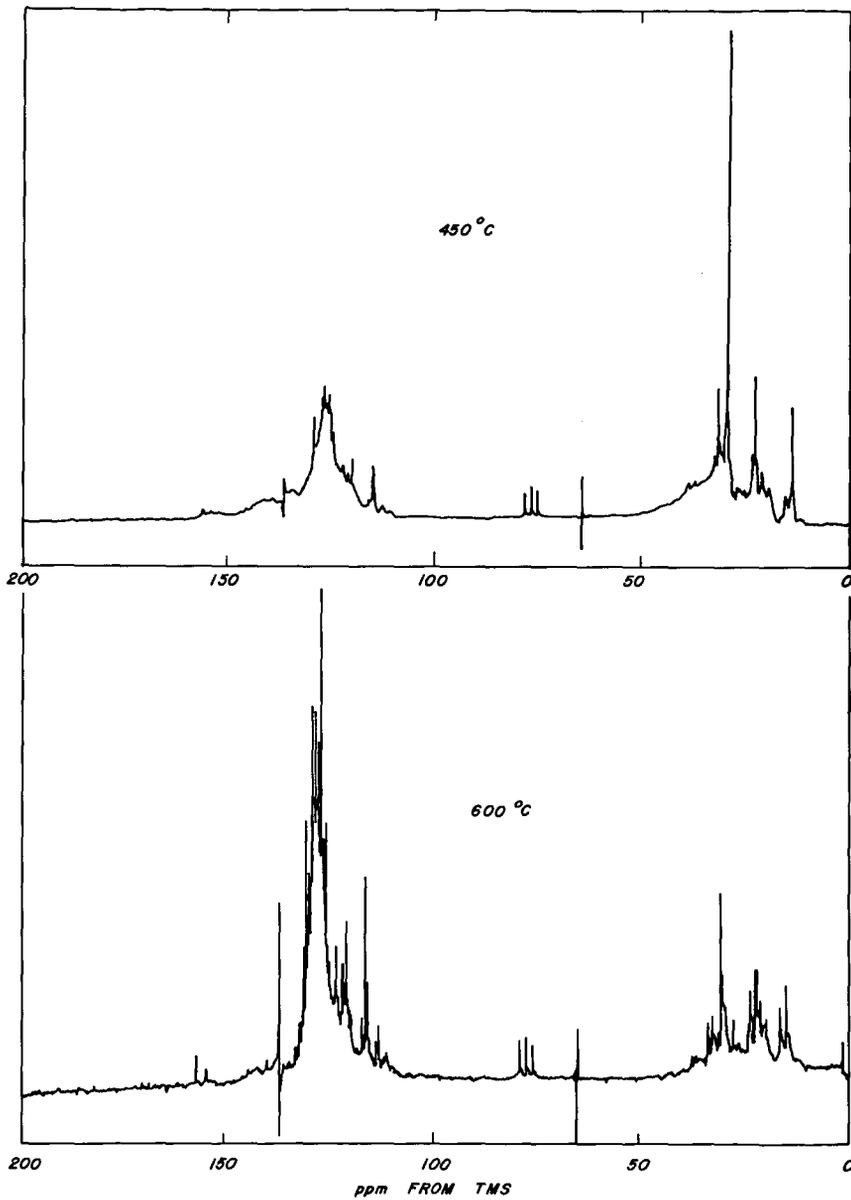


FIGURE 6  $^{13}\text{C}$  n.m.r. SPECTRA OF OILS.