

CHARACTERIZATION OF LIGHT OILS FROM LIQUEFACTION OF LIGNITE

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Introduction

Liquefaction of North Dakota Beulah seam lignite (Table 1) was carried out in a 2.3 kg coal/hr continuous processing unit at the Grand Forks Energy Technology Center. The design and engineering details of this unit have been described previously (1). Light oil (BP<300°C @ 27.5 MPa) which accounted for about 19% of the yield calculated on a MAF coal basis was withdrawn at the end of each pass and not added back to the recycle solvent. Slurry was prepared for each recycle pass by adding 30% by weight, pulverized (100% minus 60 mesh) as received (~30% moisture) lignite to the heavy product (BP>300°C @ 27.5 MPa) containing unreacted lignite and ash as well. Slurry feed rate to a 4.55 liter autoclave acting as a continuous stirred tank reactor (CSTR) at 2.3 kg/hr gave a nominal residence time of one hour. CO and H₂ gas (1:1) were added at 14.2 l/min. The pasting solvent for the first pass was redistilled anthracene oil (BP 296°C @ 1.3 Pa). The light oil sample studied was collected on the 24th recycle pass, and represents an essentially lined-out steady state product. A description of the detailed reactor conditions and of the composition of the other products was given by Farnum, Knudson and Koch (2).

Experimental

Separations

The light oil was condensed from the gases after depressurization via two let-down valves into a water cooled product receiver, separate from the heavy product let-down. The water vapor that condensed with the oil was separated in a separatory funnel.

The oil was further fractionated by extraction using the scheme suggested by Fruchter et al. (3) modified by the use of *n*-pentane rather than iso-octane. A flowsheet of the method with the percent recovery of each fraction is given in Figure 1. The number of components determined by capillary GC using a 50-meter OV-101 glass column (Table 2) indicates that the total detectable number of components is less than 277 since there is some overlap between fractions. There are less than 85 components above 1% in this lignite conversion product.

Separations of the four fractions using reverse phase HPLC with a MeOH-H₂O gradient (Altex Model 420) produced major component separations. The light oil was fractionated using the scheme of Dooley et al. (4), yielding fractions including weak acids, phenolics, basics, hydrocarbons and heteroaromatics. Gradient HPLC separation of the weak acids gave approximately 40 peaks; the phenolics, 45 peaks; and the basics, 36 peaks. The hydrocarbon fraction was resolved into 30 compounds. This separation was developed for use as an analytical scale separation technique with automatic fraction collection.

Analyses

Elemental and water analyses of the oil and the four fractions were carried out by combustion (C,H,N,S), Karl Fischer titration (H₂O), and neutron activation and

coulometry (O) (Table 3). The fractions were dried over anhydrous magnesium sulfate before analysis.

Spectroscopy

IR spectroscopic analyses were carried out on thin films of the oils between NaCl disks using a Perkin-Elmer 283* IR spectrometer.

UV studies were conducted using appropriate dilutions of the light oil and its fractions in CH_2Cl_2 . The Perkin-Elmer Hitachi model 340 with Data Handler was used either in the absorbance mode or programmed for the fourth derivative mode.

^1H NMR spectra were taken at 200 MHz with a Varian XL-200. The solutions were diluted 1:8 with CDCl_3 containing 1% of TMS. They were pulsed 25 times at flip angles of 45° or 90° . The integrated areas are shown in Table 4.

^{13}C NMR spectra were also acquired with the Varian XL-200, operating at 50 MHz using the broad band probe. The solutions were 30% oil in CDCl_3 with 1% TMS and 5×10^{-3} M $\text{Cr}(\text{AcAc})_3$. The pulse angle was 60° with 5000 to 15,000 pulses accumulated before integration. The results are presented in Table 5.

Trifluoroacetic Acid - Hydrogen Peroxide Oxidations

A trifluoroacetic acid - hydrogen peroxide oxidation (5) of the light oil was carried out. The resulting acids were derivatized to the *p*-bromophenacyl esters (6) to provide UV absorbance. They were then separated by solvent gradient ($\text{MeOH}-\text{H}_2\text{O}$) reverse phase HPLC and identified by comparison with the same sequence carried out with standards.

Results and Discussion

Basic Fraction

The basic fraction, 5% of the total, is dark in color, with heterocyclic character. The ^1H NMR has several resonance lines between 8.2 and 8.6 ppm as well as a large area between 6.5 and 7.8 ppm indicating pyridines. Some prominent lines between 2 and 3 ppm suggest methyl substituents. The IR contains all of the pyridine - quinoline stretching frequencies and also indicates ring substitution. As was expected, a very broad band appears in the NH , $\text{N}-\text{H}$ stretching region. The richly populated ^{13}C NMR spectrum of this fraction, however, shows a complex mixture of carbon types from 115 ppm to 160 ppm. Pyrroles, if present, are probably substituted since no ^{13}C peak is seen at 106-108 ppm. Indoles are possible.

Phenolic Fraction

The phenolic fraction, 25%, appears to be mainly phenols with cresols and other substituted phenols present in wide variety. Naphthols, if present, are a minor component.

The IR of this fraction, in addition to a broad OH stretching vibration, has a prominent C-H stretching vibration. The other characteristic bands of phenol are all present.

The UV (Figure 2) shows a maximum near 275 nm that is the absorption due to phenols. The fourth derivative UV (Figure 3) is well defined giving a characteristic pattern with a peak corresponding to the absorbance at 275 nm after wavelength correction.

Heteroaromatic Fraction

The ^1H NMR of the heteroaromatic fraction, 22%, (Figure 4b) is dominated by symmetrical multiplets at 7.8 and 7.5 ppm which are characteristic of naphthalene. The ^{13}C NMR (Figure 6a) shows two peaks of similar area at 127.8 and 125.7 ppm with a peak at 133.4, agreeing well with the assumption that unsubstituted naphthalene is present. The IR supports this assumption also in that the spectrum closely resembles that of naphthalene and the methylnaphthalenes with all of the frequencies represented. The weak N-H frequency in the IR along with the nitrogen present in the elemental analyses indicates that carbazoles may be present in this fraction. The ^1H and ^{13}C NMR, UV (Figures 2,3) and IR also suggest the presence of phenanthrenes.

All of the sulfur-containing compounds are present in this fraction (Table 3). Aromatic ethers are also indicated; however, no evidence of aliphatic ethers is seen.

Hydrocarbon Fractions

The hydrocarbon fraction is almost one-half of the light oil by weight. It is apparently a mixture of aliphatic molecules with some aromatic character, probably benzenoid substitution. The material is light in color, does not have an unpleasant odor, and is low boiling. The IR of the hydrocarbon fraction is very simple, dominated by the C-H aliphatic stretching frequencies and the CH_3 and CH_2 bending vibrations at $1465\text{--}1450\text{ cm}^{-1}$ and 1380 cm^{-1} . The major CH_2 rocking vibration appears at 745 cm^{-1} , $(\text{CH}_2)_2$. The aromatic C-C stretching is weakly represented at 1495 cm^{-1} .

The ^1H and ^{13}C NMR (Figure 6b) spectra are the simplest spectra seen for any of the four fractions. The aromatic protons are 15% of the total number of protons with the measured $C_{\text{ar}}/C_{\text{total}} = 0.33$ (Tables 4 and 5).

Unseparated Light Oil 28-14

The fourth derivative UV was used to compare the oil with its separated fractions. The two main UV-absorbing fractions, the phenolic and heteroaromatic fractions (Figure 2), show characteristic fourth derivative fingerprints (Figure 3). This characteristic fine structure of the fourth derivative UV is easily seen in the pattern for the complete light oil LO 28-14. The absorption near 275 nm is the main phenolic band which increases in concert with the increase in phenolic content as line-out is approached. Since the fourth derivative follows Beer's Law, the changes seen as the process proceeds may be quantitatively measured.

IR studies of the CH stretching region in the oil itself along with ^1H NMR are also very useful for monitoring the approach to line-out. The asymptotic approach of the IR ratio to a constant value as a function of recycle passes indicates that a lined-out product was obtained (2).

Trifluoroacetic acid - hydrogen peroxide oxidation of the light oil was carried out. Reverse phase solvent gradient HPLC was used to qualitatively separate the *p*-bromophenacyl esters of the acids formed during the oxidation. The following diacids were inferred from comparison with standards: 2C, 3C, 4C, 5C and 10C. Also seen were acetic, butanoic, pentanoic, cyclohexenecarboxylic and cyclohexylacetic acids.

Summary

The light oil 28-14 was separated into four fractions. The basic fraction was heterocyclic in nature containing most of the nitrogen compounds from the oil. The phenolic fraction was shown to be mostly phenols with naphthols only a minor consti-

tuent. The phenolic fraction is about 25% of the total weight of oil. The hetero-aromatic fraction, 22%, contains few components with more than three rings. It is largely composed of naphthalene and naphthalene derivatives, probably some aromatic ethers, neutral or slightly acidic nitrogen compounds and all of the sulfur compounds. The hydrocarbon fraction is the major fraction, 48%. It has no functionality as the elementary analysis shows no O, N or S. This fraction is aliphatic in nature with some benzenoid substituents.

In addition to the observed yield distribution approaching a constant value, which is one indication of line-out, by monitoring the aromatic to aliphatic proton ratio as a function of recycle pass number with IR or NMR spectrometry, the approach to constant composition can be determined.

Acknowledgement

We would like to express our appreciation to Dr. Warren Reynolds for the capillary GC separations.

* Reference to specific brand names and models is done to facilitate understanding and neither constitutes nor implies endorsement by the Department of Energy.

References

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TABLE 1. - Analyses of Coal for Beulah 3, North Dakota, Lignite

Basis of reported analysis:	Coal Analysis (GF-79-2147)		
	As-received	Moisture-free	Moisture- and ash-free
Proximate analysis, pct.:			
Moisture	29.48	--	--
Volatile matter	30.21	42.84	50.53
Fixed carbon	29.58	41.94	49.47
Ash	10.73	15.22	--
TOTAL	100.00	100.00	100.00
Ultimate analysis, pct.:			
Hydrogen	6.20	4.15	4.89
Carbon	42.87	60.79	71.71
Nitrogen	0.48	0.68	0.80
Oxygen	37.91	16.59	19.57
Sulfur	1.81	2.57	3.03
Ash	10.73	15.22	--
TOTAL	100.00	100.00	100.00

* An "atypical" Beulah Lignite chosen specifically for its high ash content.

TABLE 2. - Capillary G.C. analysis of LO 28-14 fractions

Fraction	# Components			
	>1%	0.5-1.0%	0.25-0.5%	Total
Basic	12	7	21	48
Phenolic	26	23	10	84
Heteroaromatic	21	18	19	124
Hydrocarbon	26	14	20	121

TABLE 3. - Elemental analysis of light oil 28-14
and its fractions based on LO as 100%

	<u>% C</u>	<u>% H</u>	<u>% O</u>	<u>% N</u>	<u>% S</u>	<u>% H₂O</u>
28-LO-14	84.34	10.69	0.37	3.70	0.22	0.23
Basic	19.94	2.64	0.09	3.35	0.01	--
Phenolic	19.77	2.49	0.25	0.03	0.01	--
Heteroaromatic	22.38	2.21	0.035	0.32	0.20	--
Hydrocarbon	22.26	3.35	0.001	0.00	0.01	--

TABLE 4. - ¹H NMR areas for 28-LO-14
and fractions, CDCl₃, TMS

<u>Fraction</u>	<u>% Har</u> (8.8-5.7 ppm)	<u>% Hα</u> (4-1.9 ppm)	<u>% Ho</u> (1.9-0.3 ppm)	<u>% Hphe</u> (varies)
28-LO-14	23.1	23.0	53.3	--
Basic fraction	34.1	34.1	31.8	(part of Har)
Phenolic fraction	31.3	32.3	25.9	10.5
Heteroaromatic fraction	48.1	29.0	22.5	--
Hydrocarbon fraction	15.3	19.0	65.7	--

TABLE 5. - Integrated ¹³C areas for LO 28-14 and fractions

<u>Fraction</u>	<u>Car/Ctotal</u>	<u>Car/Caliph</u>
LO 28-14	0.45	0.83
Basic fraction	0.56	1.30
Phenolic fraction	0.66	1.93
Heteroaromatic fraction	0.81	4.24
Hydrocarbon	0.33	0.49

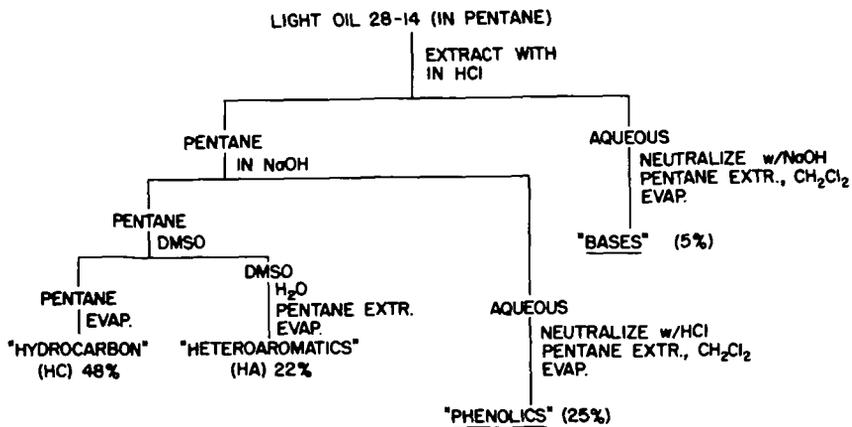


FIGURE 1. - Separation and recovery of the light oil fraction by extraction

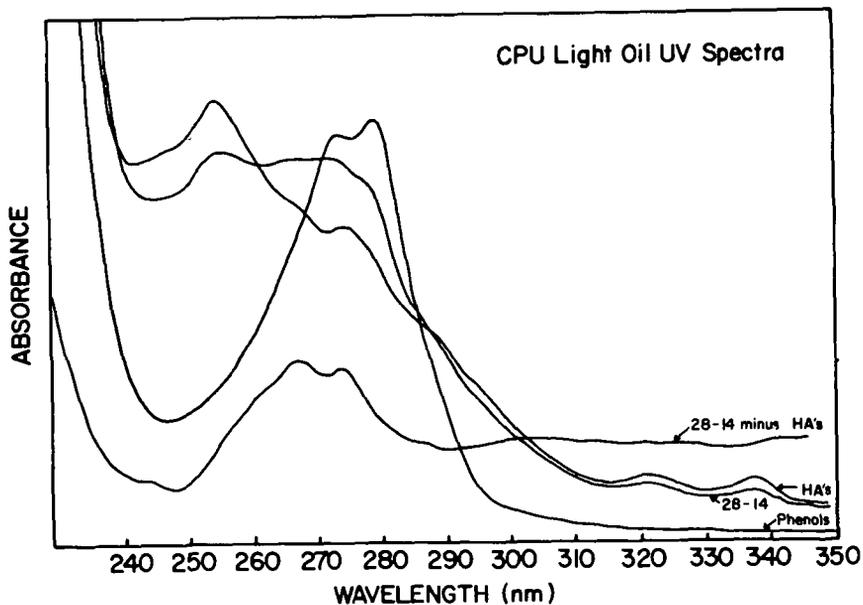


FIGURE 2. - UV spectra of LO 28-14 and fractions

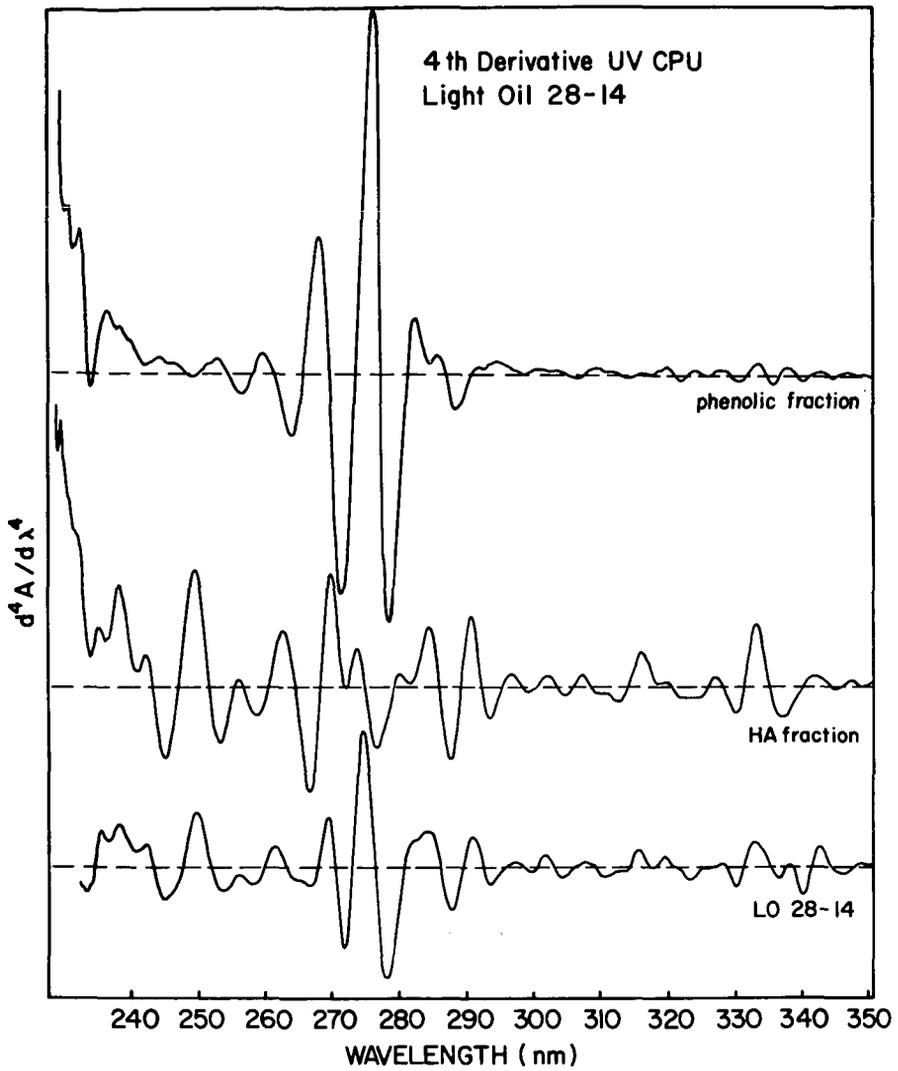


FIGURE 3. - Fourth derivative UV of light oil 28-14 and fractions

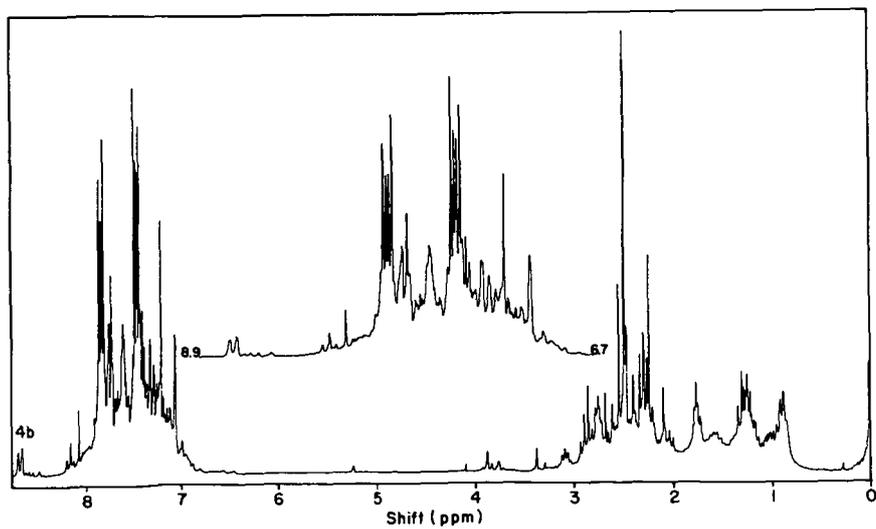
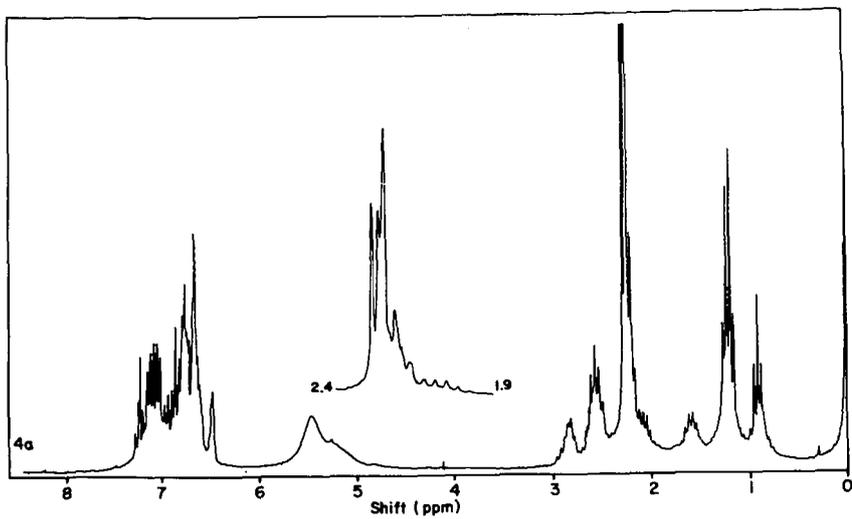


FIGURE 4. - 200 MHz ¹H NMR of light oil 28-14, a) phenolic fraction, b) heteroaromatic fraction

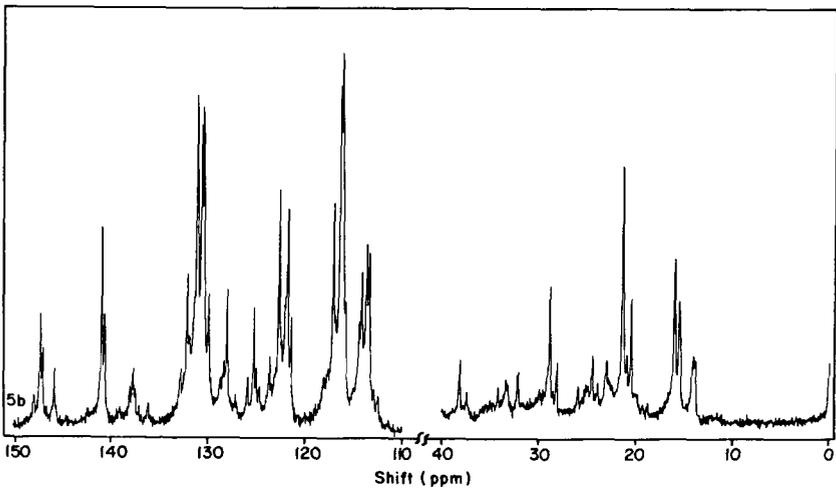
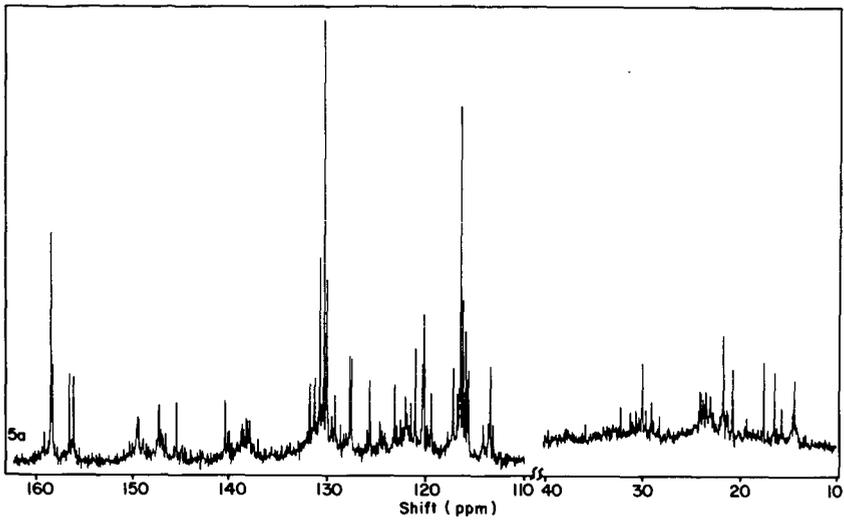


FIGURE 5. - 50 MHz ^{13}C NMR of the aliphatic and aromatic regions of light oil 28-14 (without NOE, $\text{Cr}(\text{AcAc})_3$, CDCl_3), a) basic fraction, b) phenolic fraction

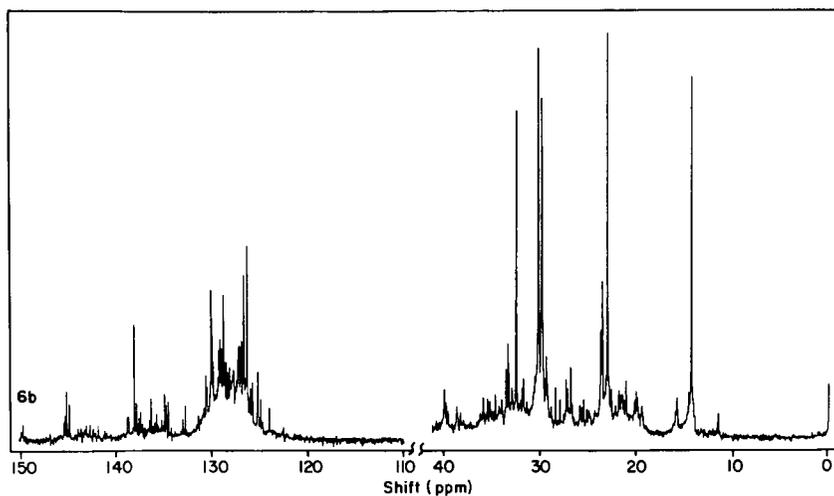
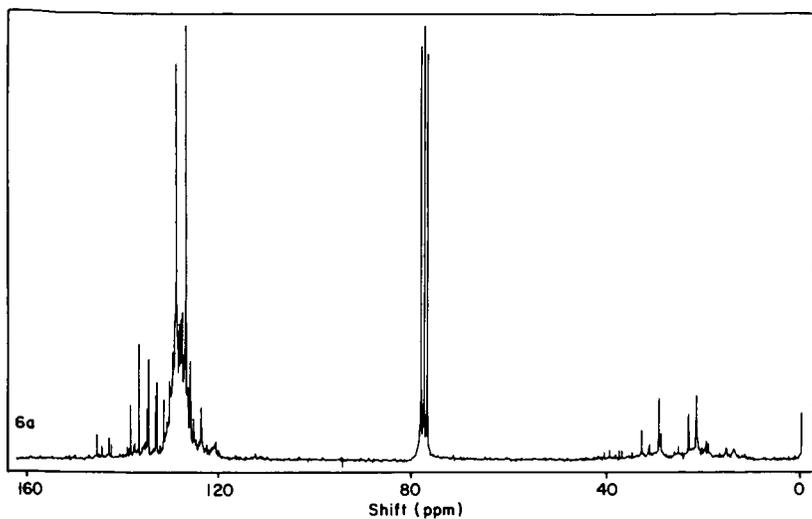


FIGURE 6. - 50 Mz ^{13}C NMR, a) of the heteroaromatic fraction, completely proton decoupled in CDCl_3 , b) aliphatic and aromatic regions of the hydrocarbon fraction (without NOE, $\text{Cr}(\text{AcAc})_3$, CDCl_3), of light oil 28-14