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CHEMICAL CHANGES IN NITROGENOUS MATERIALS
DURING HYDROCRACKING OF ATHABASCA BITUMEN

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CHEMICAL CHANGES IN NITROGENOUS MATERIALS DURING HYDROCRACKING OF ATHABASCA BITUMEN

by

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INTRODUCTION

The nitrogenous materials in synthetic crude oils are of considerable importance because they deactivate the catalysts in refining processes, e.g., desulphurization, hydrogenation, aromatization, etc. This report is an investigation of these nitrogenous compounds in synthetic crude oils obtained from Athabasca bitumen at various severities of non-catalytic thermal hydrocracking.

In a previous report (1) we described the concentration of these compounds on ion exchange resins by a modification of USBM-API 60 methods (2,3,4). In this report these modified separation techniques are applied.

Bunger (5) made extensive separations of various nitrogenous components in characterization of Utah tar sand bitumen. More recently McKay et al. have made extensive studies of nitrogenous concentrates obtained by chromatography on ion exchange resins of some petroleum fractions (6) and asphaltenes (7).

EXPERIMENTAL

Hydrocracking

The hydrocracking was done in the pilot plant of the Bitumen Processing Section of the Energy Research Laboratories. This has been described in several reports (8,9). Athabasca bitumen and hydrogen are fed into the bottom of a vertical reactor and the products, both liquid and vapour, flow from the top to a hot separator. The relatively heavy products are withdrawn from the separator and the lighter products are swept with gases to a cold receiver in which the lighter products condense and are withdrawn continuously. The uncondensed gas is oil-scrubbed to remove most of the gaseous

hydrocarbons, ammonia and hydrogen sulphide, and then recycled with fresh make-up hydrogen.

Samples: Athabasca Bitumen

Obtained from the Great Canadian Oil Sands hot water separation process.

Hydrocracked Products

Three of the products studied were obtained under steady state conditions of 2000 psi pressure, liquid hourly space velocity of 2 and temperatures of 410°C, 430°C and 460°C. The amount of pitch (residue boiling higher than 524°C) converted in these products to lighter material was 26, 49 and 79%, respectively.

Another product was obtained at 3500 psi, space velocity of 2 and 470°C. The pitch conversion in this case was 89.1%. These samples are referred to in the text by the numbers 1 to 4 respectively.

Preparation of Hydrocracked Products - Figure 1

The light oil products (obtained from the cold receiver) were topped to 200°C, asphaltenes were precipitated from the heavy oil products with 20 volumes of pentane, and then extracted with pentane. The topped light oil and the deasphaltened heavy oil products were combined proportionally to represent the deasphaltened total product topped to 200°C.

Separations - Figure 1

The separations were carried out on activated anion (Amberlyst A-29, 46.0 g) and cation (Amberlyst A-15, 56.0 g) exchange resin columns as described in an accompanying report (1). The columns were connected in series with the anion exchange resin column first in the series. After introduction of the samples (ca, 20 g), it was eluted with limited amounts of pentane (360 ml) and cyclohexane (220 ml). The columns were then disconnected and the anion exchange column eluted with benzene (220 ml), 60% benzene-40% methanol (120 ml) and 80% benzene-20% acetic acid (160 ml). These are referred to as anion eluents AI, AII and AIII, respectively. The cation ex-

change column was eluted with benzene (120 ml), 60% benzene-40% methanol (80 ml) and a benzene-methanol mixture containing 8% isopropylamine, 37% methanol, 55% benzene (140 ml) followed by benzene. The fractions eluted by these solvents are referred to as eluates CI, CII and CIII, respectively.

Analyses

Nitrogen Analyses

Nitrogen determinations were obtained using a Dohrmann microcoulometer on fractions diluted with toluene.

Infrared Spectroscopy

The absorbance of the various fractions in the regions 1600-1800 cm^{-1} and 3300-3800 cm^{-1} were obtained in methylene chloride solutions with the use of a Beckman model IR-12 spectrometer (2). The amounts of pyrrolic functions were determined by taking area measurements of the absorbances peaking around 3465 cm^{-1} and using appropriate base lines. For the pyrrolic functions the absorbance of carbazole was used as a reference.

Titration of Basic Nitrogen Compounds

The bases were titrated potentiometrically according to the method described in Ref. 10 and 11, and modified by Buell (12).

RESULTS AND DISCUSSION

The distribution of total nitrogen content in the hydrocracked products and the combined sample that has undergone further separation on the ion exchange column is shown in Table 1.

TABLE 1

Distribution of Total Nitrogen Content
In Hydrocracked Athabasca Bitumen Products

Sample Number	Nitrogen Content, wt %	Nitrogen Content, wt %			
		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Pitch conversion	wt %	26	49	79	89
Light oil, below 200°C		0.010	0.013	0.046	0.066
Light oil, above 200°C		0.081	0.112	0.107	0.199
Topped deasphalted sample		0.356	0.374	0.380	0.346
Asphaltenes		1.30	1.62	1.90	2.23

Chromatography on Ion Exchange Resins

The results that were obtained by separation of the different samples obtained at various levels of pitch conversion are shown in Table 2.

TABLE 2

Per Cent by Weight Fraction Distribution
in the Bitumen Feed and its Hydrocracked Product

<u>Sample</u>	<u>Feed</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Pitch Conversion		26	49	79	89
Gases	-	-	4.17	8.61	11.50
Light Ends (<200°C)	-	3.88	8.26	13.01	14.81
Pentane eluate	60.5	59.5	60.8	58.9	56.9
Cyclohexane eluate	2.76	1.85	1.06	1.39	2.62
Anion eluate, AI	4.97	4.48	4.34	3.92	1.80
AII	3.63	2.31	2.44	2.53	2.43
AIII	3.39	1.21	0.85	0.38	0.84
Cation eluate, CI	2.33	2.70	2.80	1.89	1.03
CII	2.58	1.29	1.42	1.01	0.69
CIII	2.32	2.20	2.32	1.14	1.02
Asphaltenes	17.2	17.0	9.8	7.2	4.34

The amount of pentane eluate does not vary much due to hydrocracking, in spite of the increase in light ends. If there is any loss of the pentane eluate to the light ends it appears to be compensated for by the addition of hydrocarbons and sulphur compounds produced from other components. As the extent of hydrocracking increases, the molecules with functional groups decrease and therefore the fractions retained on the ion exchange resins become smaller in weight. The diminution of the asphaltenes also contributes to other fractions. Most of the changes, however, appear to occur in the more severely treated products.

The nitrogen contents of the eluates and the total amount of the nitrogen that each fraction contributes to 100 g of bitumen and its products are shown in Tables 3 and 4.

TABLE 3

Nitrogen Content (wt %) of the Fractions

<u>Sample</u>		<u>Feed</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Pitch Conversion	wt %	-	26	49	79	89
Pentane Eluate		0.028	0.01	0.01	0.018	0.01
Cyclohexane Eluate		0.46	0.71	0.67	0.21	1.53
Anion Eluate, AI		1.96	3.33	3.18	2.56	3.39
AII		1.12	1.42	1.85	3.43	2.83
AIII		0.59	1.61	1.30	2.73	-
Cation Eluate, CI		0.89	1.18	1.25	0.37	2.88
CII		0.56	1.43	1.50	1.21	1.16
CIII		2.50	2.27	3.15	3.49	3.77
Asphaltenes		1.40	1.30	1.62	1.90	2.23

TABLE 4

Amounts of Nitrogen (grams) in the Fractions
from 100 grams of Bitumen and Hydrocracked Products

<u>Sample</u>		<u>Feed</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Pitch Conversion	wt %	-	26	49	79	89
Pentane Eluate		0.017	0.007	0.007	0.011	0.006
Cyclohexane Eluate		0.013	0.014	0.007	0.003	0.042
Anion Eluate, AI		0.097	0.155	0.142	0.100	0.093
AII		0.041	0.034	0.045	0.087	0.014
AIII		0.020	0.020	0.011	0.013	-
Cation Eluate, CI		0.021	0.033	0.036	0.007	0.031
CII		0.014	0.019	0.022	0.012	0.008
CIII		0.058	0.052	0.075	0.040	0.040
Asphaltenes		0.240	0.229	0.163	0.137	0.100

The amount of nitrogen retained on the anion exchange resins increases from 0.158 g to 0.209 g/100 g of sample during the least severe treatment. There is little change in this amount in more severe treatments except in the case of the most severely treated products. The amount of nitrogen in the AI fraction increases in sample 1 but then decreases in the other samples with increasing severity. In the AII fractions, the situation is reversed

except for the most severely cracked sample. This is related to infrared absorption at 1665-1680 cm^{-1} as discussed later.

In the AIII eluate the amount of nitrogen does not appear to be affected by the least severe treatment but with more severe treatment it decreases. For the total materials retained on the anion exchange resins there is an increase during the least severe treatment and the amount of nitrogen in Samples 1, 2 and 3 is fairly constant, but decreases markedly in Sample 4.

The amount of nitrogen in fractions retained on the cation exchange resin increases with sample 1 and sample 2 but then declines sharply. According to titration discussed later it appears that some very basic material is lost on the resins in the case of the highly cracked samples.

There is a steady drop in the total amount of nitrogen in asphaltenes with increasing severity. However, the nitrogen concentration increases.

Infrared Spectroscopy

Anion Exchange Resin Eluates

The 1600-1800 cm^{-1} region was scanned (Fig. 2). The absorption at 1655 cm^{-1} is attributed to 2-quinolones of these compounds as shown by the spectrum of its AII fraction. This absorption shows also in the AI fraction of the least severely hydrocracked sample. But with the increase in hydrocracking these compounds become diminished to trace amounts. It was also noticed that hydrocracking has caused some changes in these compounds so that they elute in the AI fraction of Sample 1 rather than in the AII fraction as in the case of the bitumen feed.

The absorption at 1665-1680 cm^{-1} is considered to be due to amide compounds (13). This absorption is small in the spectra of the untreated bitumen fractions, but is quite evident in the AII fraction of Sample 1. The same trend is observed in Sample 3, but not in Sample 4. The AII fraction of Sample 3 has a high nitrogen content and substantial absorption in this region. The AII fraction, Sample 4, shows this peak only as a shoulder to the band at 1700 cm^{-1} , and it has a lower nitrogen content. It appears that these amides absorbing at 1665-1680 cm^{-1} are formed during hydrocracking treatments but they become degraded under the most severe treatment.

Some of the fractions have absorption peaks around 1700 cm^{-1} which is ascribed to both keto (13) and amide (6) groups. Since the keto groups are not thermally stable (14), we assume that this band in the hydrocracked

1

samples is due to certain amide compounds. This absorption is present in the bitumen fraction AI. Also, all the AI fractions of the hydrocracked samples show this absorption to various extents. In the most severely-treated sample this peak is prominent in the AII but not in the AI fraction.

The band at 1600 cm^{-1} is attributed to pyridines and related structures or to aromatic hydrocarbon groups.

Cation Exchange Resin Eluates

From scanning the $1600\text{--}1800\text{ cm}^{-1}$ region (Fig. 3), these fractions do not appear to have noticeable amounts of quinolones.

There is little amide absorption in the $1665\text{--}1680\text{ cm}^{-1}$ region in the CI fractions but all CII fractions, with the exception of Sample 4, have substantial absorption in this region. The amount of this absorption is reflected in the nitrogen contents of the CII fractions which increase during the least severe treatment from 0.56 to 1.43%. In sample 2 this absorption remains high but then falls in sample 3 and the same trend is observed in the nitrogen content. In sample 3 this absorption in CII is absent; however there is only a small drop in nitrogen content indicating that this absorption only accounts for part of the nitrogen content. The CIII fractions have no absorption in this region.

Only the CI fractions show peaks around 1700 cm^{-1} . This absorption is very strong for the CI fraction of sample 4.

Asphaltenes

The absorption in the $1600\text{--}1800\text{ cm}^{-1}$ region for the asphaltenes, Fig. 4, shows no peaks except that of the 1600 cm^{-1} . However the amount of absorption in the carbonyl region ($1650\text{--}1700\text{ cm}^{-1}$) relative to the 1600 cm^{-1} peak appears to decrease with increasing severity of hydrocracking.

Pyrrolic Compounds

Anion Resin Exchange Eluates

Peaks at 3465 cm^{-1} in the various spectra (Fig. 5) are attributed to these compounds (10). The results in Table 5 were obtained by area measurements and by using the absorptivity of carbazole as a reference compound. The bulk of these compounds appears in the AI fractions of the feed

and less severely hydrocracked samples as well as asphaltenes. With increasing severity, more appears in the All fractions.

Neutral Fractions (Cyclohexane Eluates)

A small amount of these compounds were present in the cyclohexane eluate (Fig. 5) indicating that they are neither sufficiently acidic nor basic to be retained by either of the ion exchange resins. These compounds might be indoles in which the pyrrolic function is highly hindered.

Cation Resin Exchange Fractions

The pyrrolic material (Fig. 6) retained by the cation exchange resin could be basic alkyl indoles and pyrroles, whereas the acidic carbazoles were retained on the anion exchange resin.

Asphaltenes

It is interesting that the pyrrolic absorption (Fig. 4) increases with the increase in severity of hydrocracking regardless of the decrease in the amounts of asphaltenes, Table 2. The total amount of pyrrolic compounds in the asphaltenes does not change appreciably with hydrocracking but increases at the most severe treatment.

Determination of Basicity by Titration

The basicities of the deasphaltened topped samples were 3.71, 3.92, 12.51 and 13.16 meq/100 gm for the feed and product Samples 1, 3 and 4, respectively. The neutralization points for the less severely cracked samples were insufficiently defined, contrary to the case of the extensively cracked samples. The material retained on the anion exchange resins appeared to be highly basic and was not completely eluted in the case of the severely hydrocracked samples.

TABLE 5

Milliequivalents of Pyrrolic Compounds
in 100 grams of the Bitumen and Hydrocracked Products

<u>Sample</u>		<u>Feed</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Pitch Conversion	wt %		26	49	79	89
Pentane Eluate		-	-	-	-	-
Cyclohexane Eluate		-	0.34	0.17	-	0.51
Anion Eluate, AI		1.01	2.01	3.24	2.12	1.84
	AII	0.34	0.56	0.70	1.01	3.35
Cation Eluate, CI		0.23	0.51	0.70	0.24	0.62
	CII	-	-	-	0.13	0.20
Asphaltenes		1.72	1.87	1.02	1.47	2.32

CONCLUSIONS

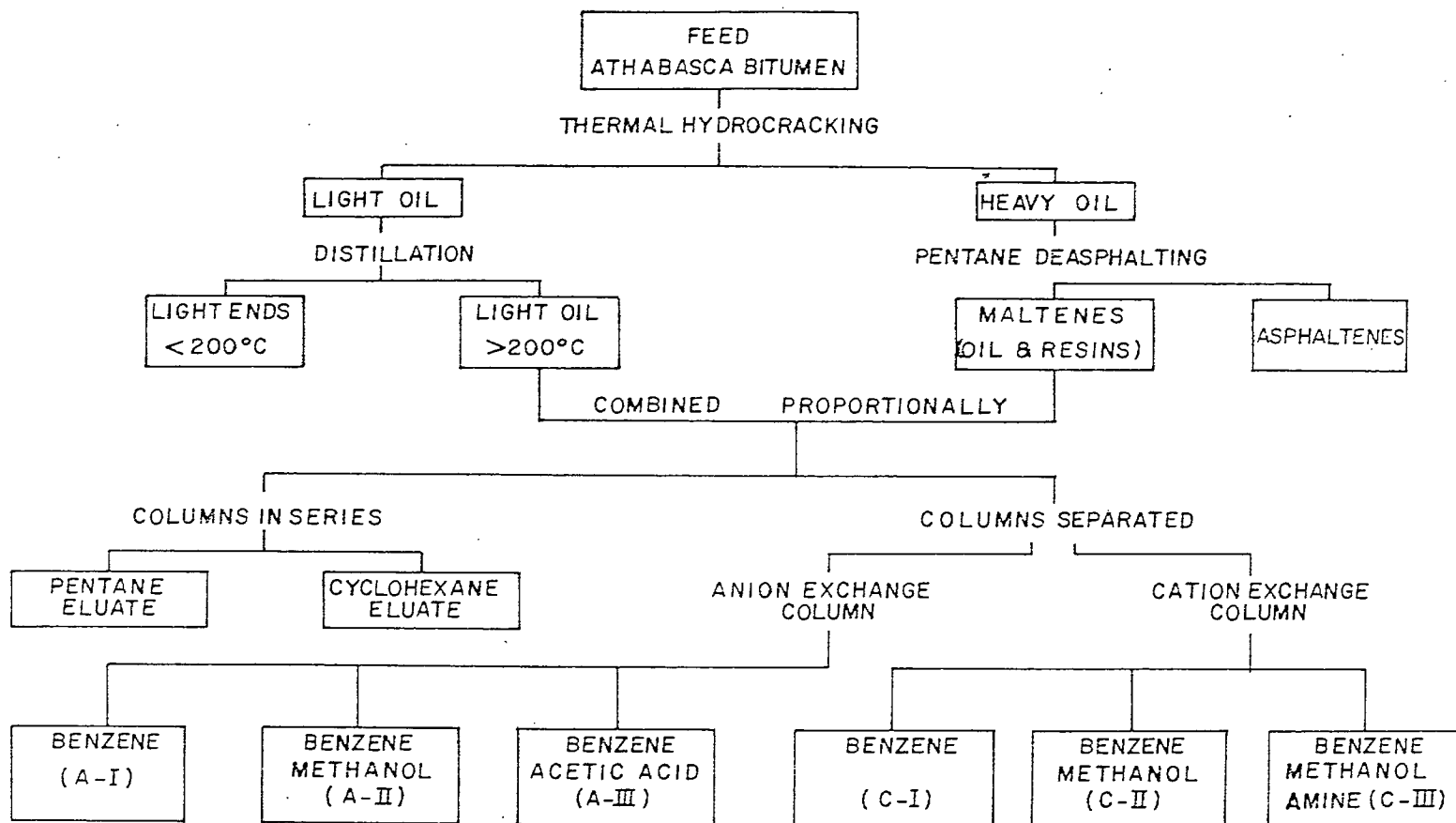
The nitrogen content increases in the liquid products of Athabasca bitumen due to non-catalytic thermal hydrocracking. Some amide compounds seem to be generated, but they diminish with severe treatment. Pyrrolic compounds increase, but the 2-quinolones that are present in the bitumen degrade to traces in the highly-cracked product.

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HYDROCRACKING AND SEPARATION (SCHEMATIC)

FIGURE I

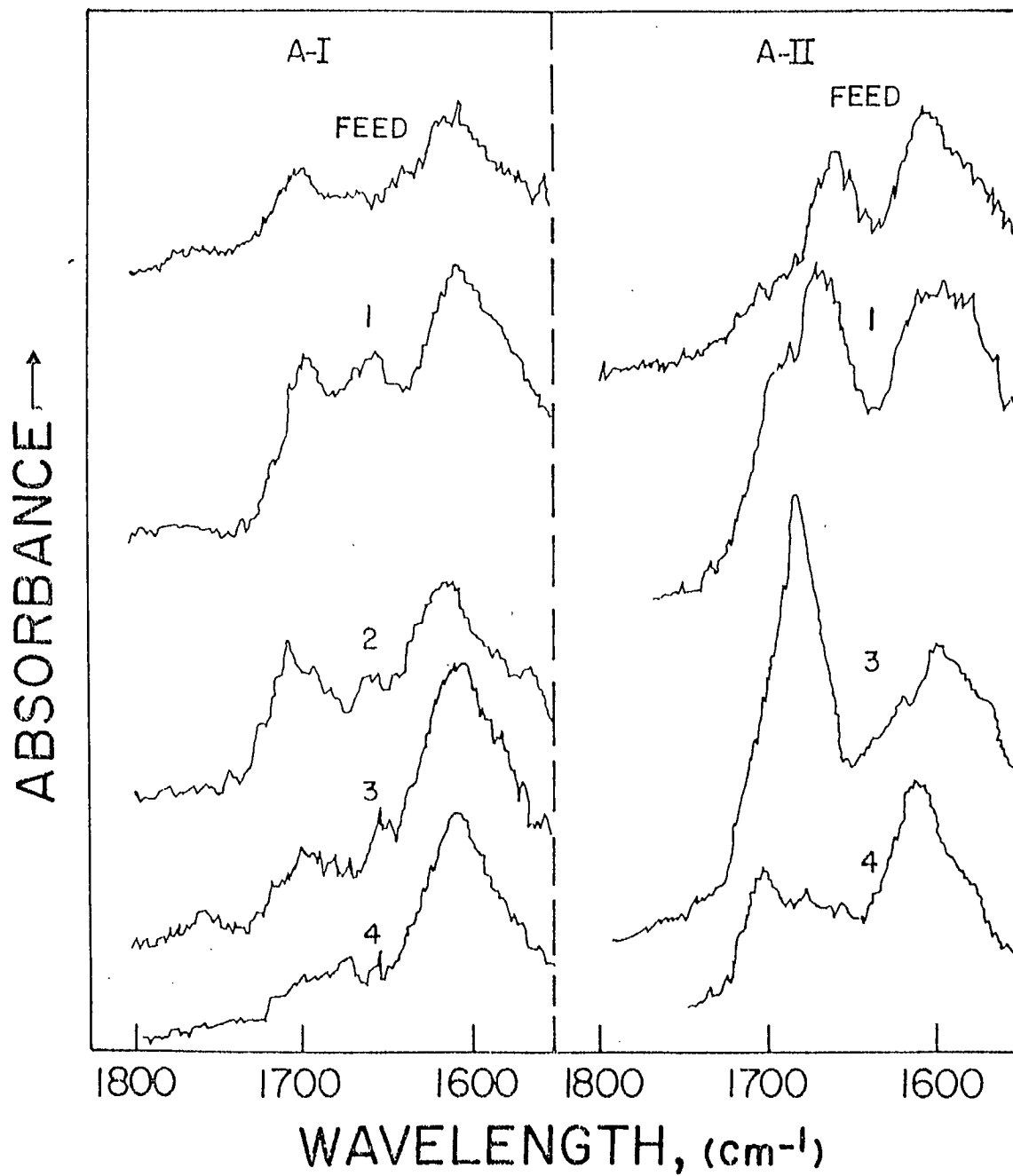


FIGURE 2 - INFRARED SPECTRA OF ANION ELUATES

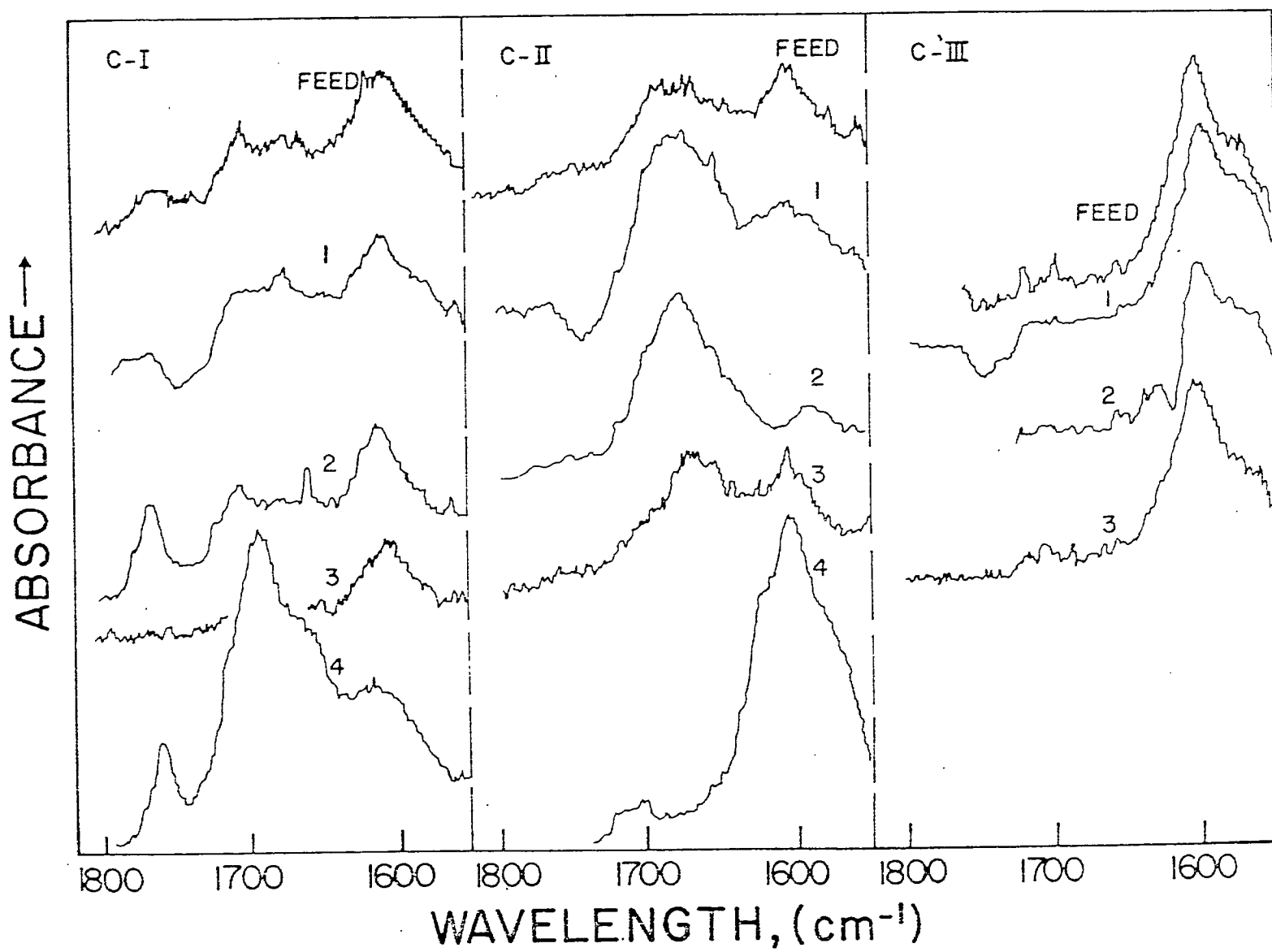


FIGURE 3 - INFRARED SPECTRA OF CATION ELUATES

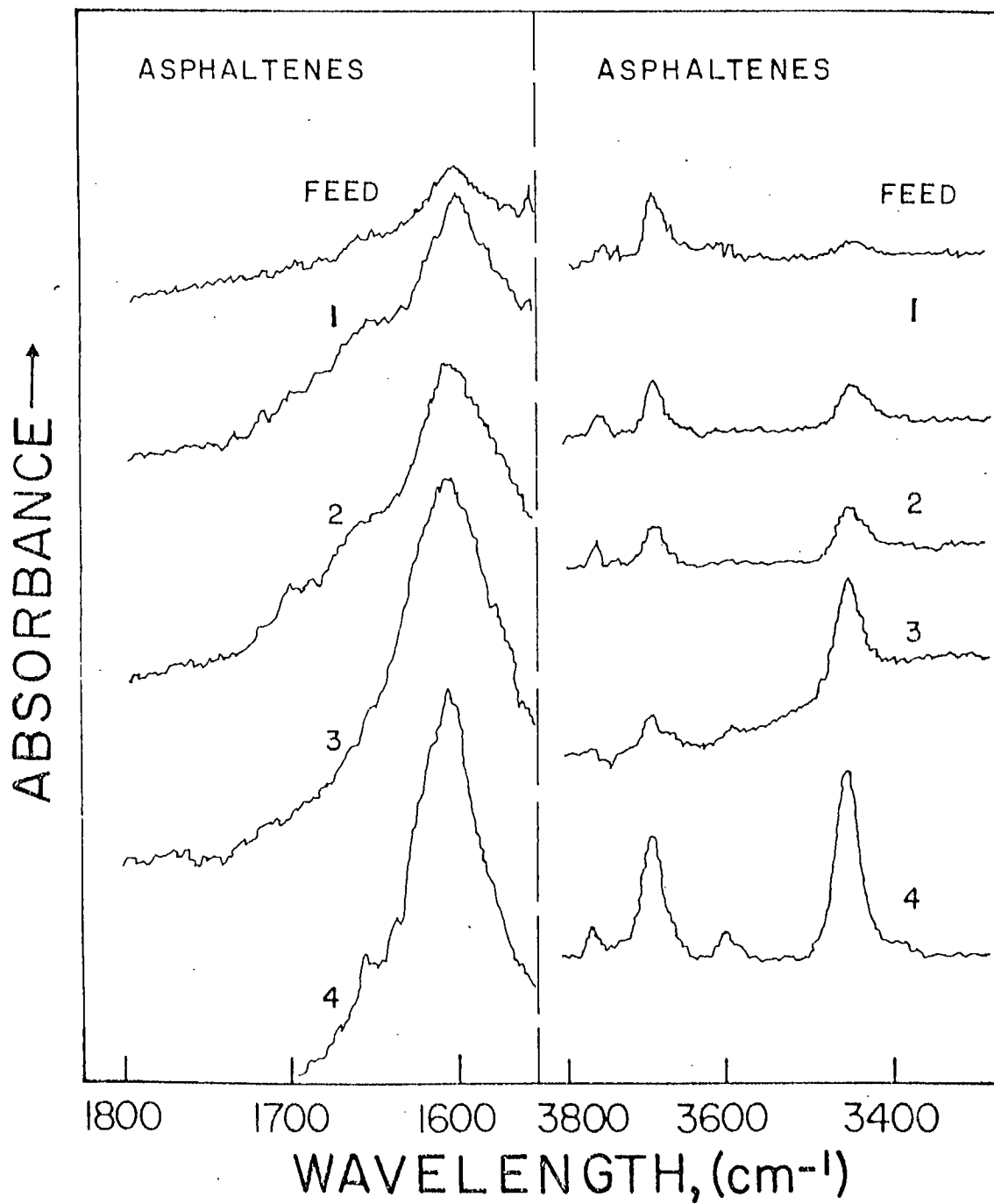


FIGURE 4 - INFRARED SPECTRA OF ASPHALTENES

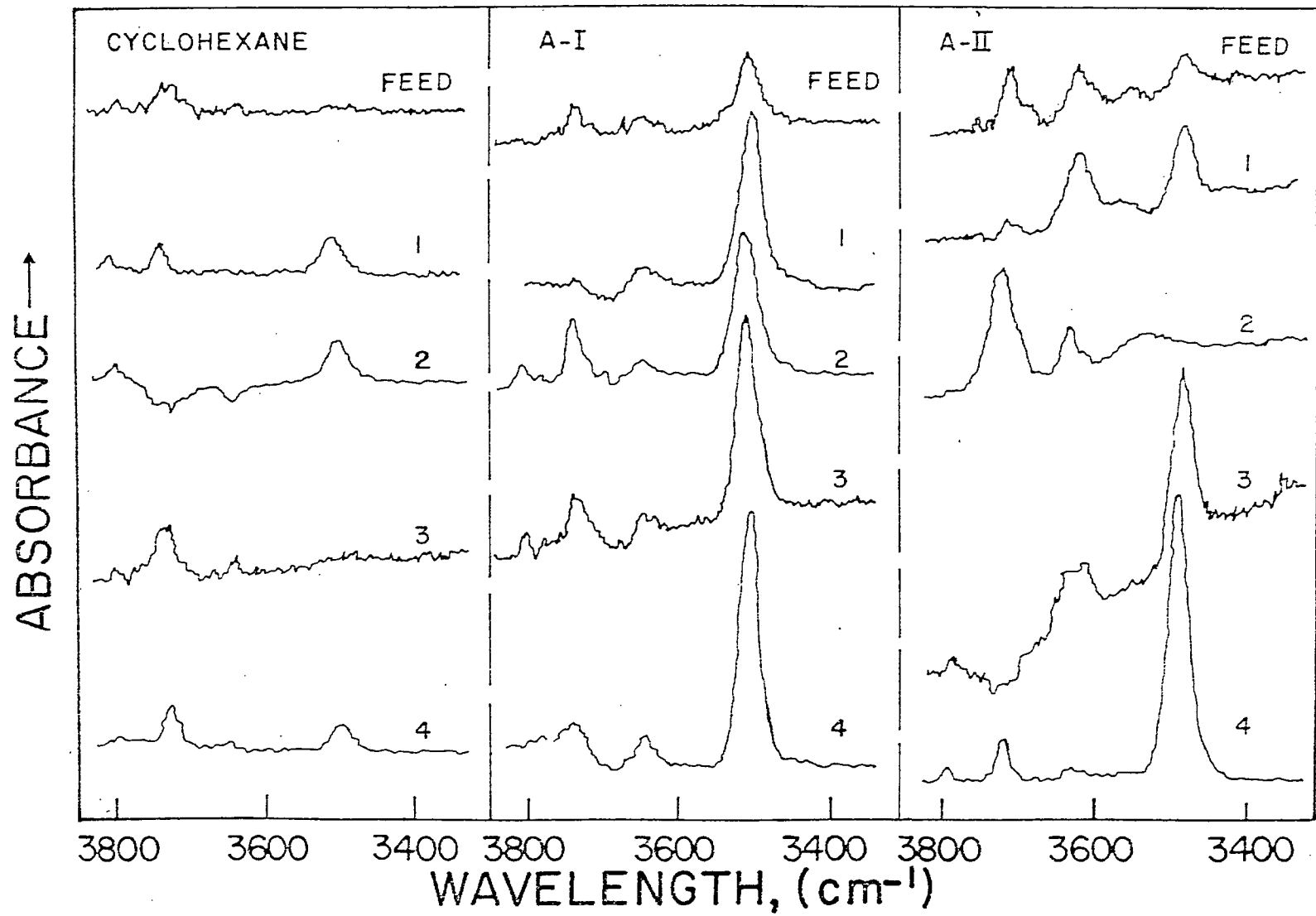


FIGURE 5 - INFRARED SPECTRA OF ANION ELUATES

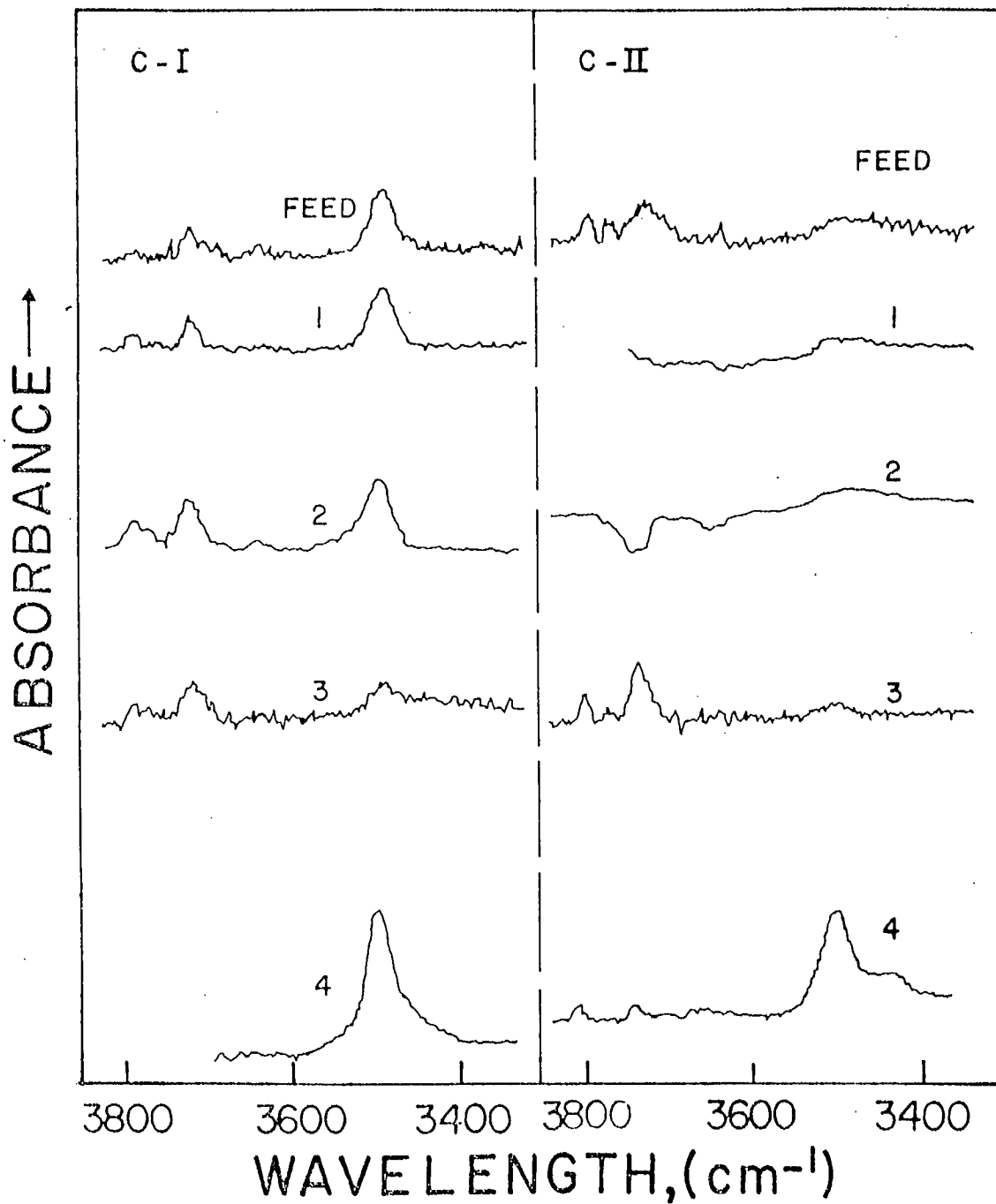


FIGURE 6 - INFRARED SPECTRA OF CATION ELUATES