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REPORT 79-20

EFFECT OF HYDROCRACKING ON THE DISTRIBUTION OF NITROGENOUS COMPONENTS IN ATHABASCA BITUMEN

H. SAWATZKY, J.E. BESHAI, G.T. SMILEY AND A.E. GEORGE

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ERRATA: Page 2, column 2, paragraph 2, sentence 1, line 4 should read ..."Bechman model 1R-12 spectrometer (8)", *not* "...(3)"

Page 6, column 1, last paragraph, line 2 should read "...these compounds (Fig. 5)(8)", *not* "...(10)"

EFFECT OF HYDROCRACKING ON THE DISTRIBUTION OF NITROGENOUS COMPONENTS IN ATHABASCA BITUMEN

by

H. Sawatzky*, J.E. Beshai**, G.T. Smiley*** and A.E.George****

ABSTRACT

The effect of hydrocracking on the distribution of nitrogenous components in Athabasca bitumen was investigated by studying products obtained at different severities. The components were separated by chromatography on anion and cation exchange resins using a modified method developed in connection with API project 60. The various fractions of nitrogenous and associated polar compounds were examined using infrared spectrometry and titration of the bases. Infrared data showed that carbazoles, indoles and related compounds, particularly in the asphaltenes increased substantially with hydrocracking severity. Basicity of the hydrocracked products which, too, increases with severity, is also discussed.

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LES EFFETS DE L'HYDROCRAQUAGE SUR LA DISTRIBUTION DES COMPOSANTES AZOTEES DANS LE BITUME D'ATHABASCA

par

H. Sawatzky*, J.E. Beshai**, G.T. Smiley*** et A.E. George****

RESUME

L'effet de l'hydrocraquage sur la distribution des composantes azotées dans le bitume d'Athabasca a été étudié en analysant les produits obtenus à différents facteurs de sévérité. Les composantes ont été séparées par la chromatographie sur les résines pour l'échange d'anion et de cation à l'aide d'une méthode modifiée mise au point dans le cadre du projet 60 de l'API. On a examiné les diverses fractions de composés azotés et autres composés polaires apparentés à l'aide de la spectrométrie infra-rouge et le tritrage des éléments basiques. Les données de l'infra-rouge ont démontré que les carbazols, les indoles et autres composés apparentés, particulièrement s'ils se trouvent dans les asphaltènes, augmentent considérablement avec la sévérité de l'hydrocraquage. On discute aussi de la basicité des produits d'hydrocraquage qui elle aussi augmente avec la sévérité.

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INTRODUCTION

In pilot-plant-scale runs the thermal hydrocracking process has been found to give a high distillate yield and to elimiate the production of waste coke in the processing of Athabasca bitumen (1). In keeping with the department's policy of ensuring maximum utilization of non-renewable resources, CANMET has supported research on hydrocracking of Athabasca bitumen. This report deals with the effect of hydrocracking severity on the distribution of nitrogenous components in the products.

The nitrogenous materials in synthetic crude oils are important because they deactivate the catalysts in refining processes, e.g., desulphurization, hydrogenation and aromatization. This report is the first in a series dealing with the effect of hydrocracking on the distribution of these compounds in the Athabasca bitumen and Canadian heavy oils. The ultimate objective of this series of studies is to provide a basis for choosing the optimal hydrocracking conditions that would produce synthetic fuels least deleterious to the catalyst in further upgrading processes. Progressive hydrocracking severity together with structural chemical analysis provide a means for step wise elucidation of the chemical composition of these nitrogenous compounds, which might be valuable commodities for use as additives to improve the characteristics of certain building materials and as binders in briquetting, etc.

A previous report described the concentration of these compounds on ion exchange resins by the modified USBM-API 60 method used in this study (2,3,4,5).

Bunger made extensive separations of various nitrogenous components in characterizing Utah tar sand bitumen (6). More recently, McKay et al. made extensive studies of nitrogenous concentrates obtained by chromatography on ion exchange resins of some petroleum fractions and asphaltenes (7,8).

EXPERIMENTAL

HYDROCRACKING

Pilot plant hydrocracking of Athabasca bitumen obtained from Great Canadian Oil Sands Limited was done at CANMET's Energy Research Laboratories and was described in previous reports (1,9). Athabasca bitumen and hydrogen are fed into the bottom of a vertical reactor from which both liquid and vapour products flow from the top to a hot separator. The relatively heavy products are withdrawn from the separator and the lighter products with gases are swept 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 is then recycled with fresh make-up hydrogen.

SAMPLES

Athabasca bitumen

Athabasca bitumen obtained from the Great Canadian Oil Sands Limited's hot water separation plant was the raw material tested.

Hydrocracked Products

Four thermally hydrocracked products referred to as samples 1 to 4 were investigated. The amount of pitch (higher than 524°C) that was converted to lighter materials in these products was 26, 49, 79, and 89%, respectively.

PREPARATION OF PRODUCTS

The light oil products obtained from the cold receiver were topped to 200°C. The asphaltenes were precipitated from the heavy oil products with 20 volumes of pentane and were then extracted with pentane (Fig. 1). The topped light oil and the deasphaltened heavy oil products were combined proportionally to represent the deasphaltened total product topped to 200°C.

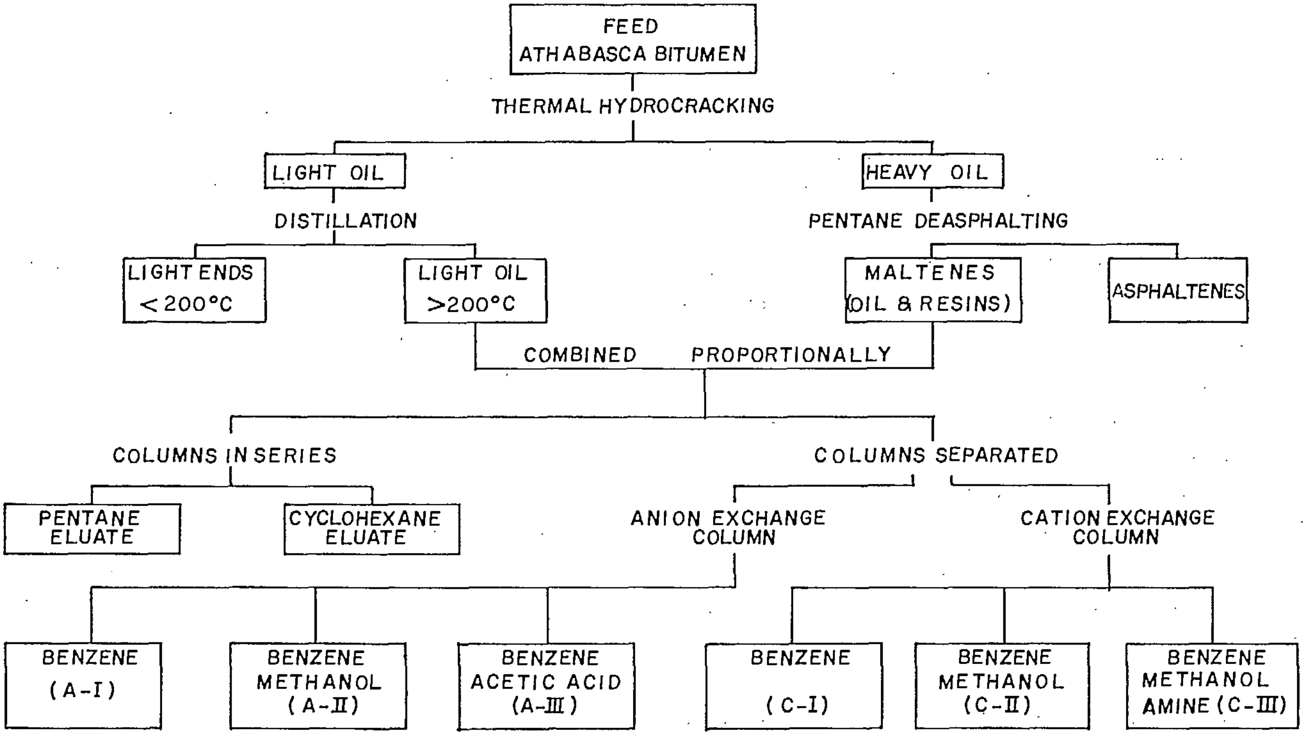

Fig. 1 - Hydrocracking and separation schematic flowsheet

SEPARATIONS

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 elsewhere (2) (Fig. 1). The columns were connected in series, with the anion exchange resin column being first. After introducing the samples of ∿ 20 g, the columns were eluted with 360 mL of pentane and 220 mL cyclohexane. The columns were then disconnected and the anion exchange column eluted with 220 mL of benzene, 120 mL of 60% benzene-40% methanol and 160 mL of 80% benzene-20% acetic acid. These three are referred to as anion eluents AI, AII and AIII, respectively. The cation exchange column was eluted with 120 mL of benzene, 80 mL of 60% benzene-40% methanol and 140 mL of benzene-methanol mixture containing 8% isopropylamine, 37% methanol, and 55% benzene, followed by benzene. The fractions eluted by these solvents are referred to as eluates CI, CII and CIII, respectively.

ANALYSES

Nitrogen

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

Infrared Spectroscopy

The absorbance of the various fractions between 1600-1800 cm^{-1} and between 3300-3800 cm^{-1} were obtained in methylene chloride solutions with a Beckman model 1R-12 spectrometer (3). 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.

Titrating Basic Nitrogen Compounds

Basic nitrogen compounds were titrated potentiometrically according to the method described by Wimer and Fritz (10,11) and modified by Buell (12).

RESULTS AND DISCUSSION

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

CHROMATOGRAPHY ON ION EXCHANGE RESINS

Results obtained by separating the different samples are shown in Table 2.

Hydrocracking does not markedly vary the amount of pentane eluate despite the increase in light ends. Any loss of the pentane eluate to the light ends appears to be compensated for by the addition of hydrocarbons and sulphur compounds produced from other components. As hydrocracking severity increases, the molecules with functional groups decrease and therefore the amount of material retained on the ion exchange resins becomes less. The diminution of the asphaltenes also contributes to the amount of other fractions. Most of the changes, however, appear to occur in the more severely hydrocracked products.

The nitrogen content of the eluates and the total nitrogen that each fraction contributes

Table 1 - Distribution of total nitrogen in hydrocracked Athabasca bitumen products

	Nitrogen (wt %)			
Product	1	2	3	4
Pitch conversion	26.0	49.0	79.0	89.0
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 deasphaltened sample	0.356	0.374	0.380	0.346
Asphaltenes	1.30	1.62	1.90	2.23

Table 2 - Fraction distribution, wt % in the bitumen feed and its hydrocracked product

	Distribution (wt %)				
Product	Feed	1	2	3	4
Pitch conversion	-	26.0	49.0	79.0	89.0
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

to 100 g of bitumen and its products are shown in Tables 3 and 4.

Nitrogen retained on the anion exchange resins increased from 0.158 to 0.209 g/100 g of sample with least severe hydrocracking. Marked change occurred only in the most severely hydrocracked product. Nitrogen in th AI fraction increased in sample 1 but then decreased in the others when severity was increased. In the AII fractions, this was reversed except for the most severely cracked sample. This is related to infrared absorption at 1665-1680 cm^{-1} and is discussed later.

In the AIII eluate the nitrogen did not appear to be affected except with more severe treatment when it decreased. For material retained on the anion exchange resins an increase occurred during the least severe treatment and the nitrogen content in samples 1, 2 and 3 was fairly constant but decreased markedly in 4.

The nitrogen in fractions retained on the cation exchange resin increased in samples 1 and 2 but then declined sharply. It appeared that some basic material was lost on the resins in

Table 3 - Nitrogen content (wt %) of the fractions

Fraction	Nitrogen (wt %)				
	Feed	1	2	3	4
Pitch conversion (wt %)	-	26.0	49.0	79.0	89.0
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 - Amount of nitrogen (g) in the fractions from
100 g of bitumen and hydrocracked products

Fraction	Nitrogen (g)				
	Feed	1	2	3	4
Pitch conversion (wt %)	-	26.0	49.0	79.0	89.0
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

highly cracked samples, which is discussed later under titration.

A steady decline occurred in the total amount of nitrogen in asphaltenes with increasing hydrocracking severity (Table 4); however its percentage concentration increased (Table 3).

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 is shown also in the AI fraction of the least severely hydrocracked sample, but with increased hydrocracking these compounds diminished to traces. It was also noted that hydrocracking caused changes in these compounds so that they elute in the AI fraction of sample 1 rather than in the AII fraction as in the bitumen feed.

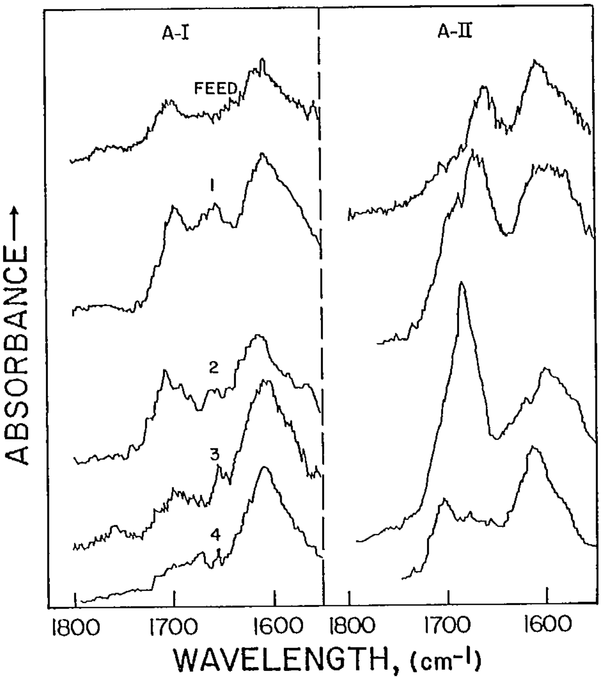

Fig. 2 - Infrared spectra of anion eluates

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

Some of the fractions have absorption peaks at about 1700 cm^{-1} which was ascribed to both keto and amide (7) groups (13,7). Because the keto groups are not thermally stable, it is assumed that this band in the hydrocracked samples was due to certain amide compounds (14). This absorption was present in the AI bitumen fraction. Also, all the AI fractions of the hydrocracked samples show this absorption. In the most severely treated sample this peak was prominent in the AII but not in the AI fraction.

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

Cation Exchange Resin Eluates

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

Little amide absorption occurred in the 1665-1680 cm^{-1} region in the CI fractions but all CII fractions, except sample 4, had substantial absorption. This absorption is reflected in the nitrogen contents of the CII fractions which increase in the least severe treatment from 0.56 to 1.43%. In sample 2 this absorption remained high but declined in sample 3 and the same trend was observed in nitrogen content. In sample 3 this absorption in CII was absent; however, only a small decline in nitrogen content occurred indicating that this absorption only accounted for part of the nitrogen content. The CIII

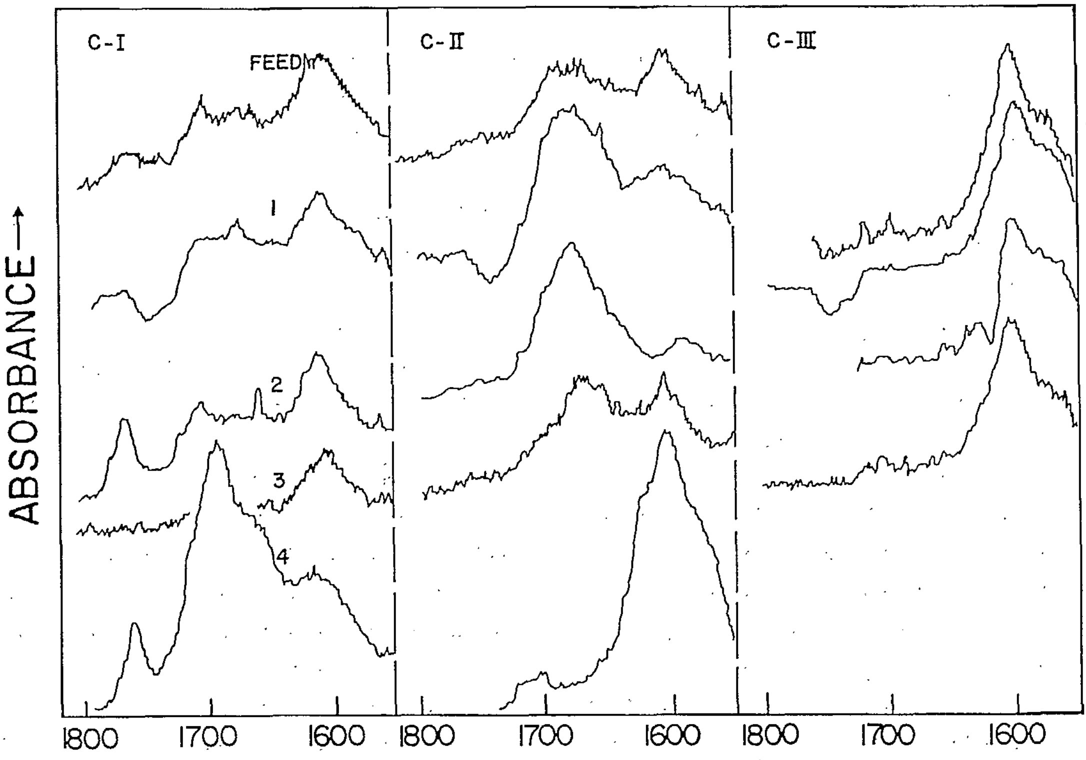

Fig. 3 - Infrared spectra of cation eluates

fractions had no absorption in this region.

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

Asphaltenes

The absorption in the 1600-1800 cm^{-1} region for the asphaltenes showed no peaks except at 1600 cm^{-1} (Fig. 4). However, the amount of absorption in the 1650-1700 cm^{-1} carbonyl region relative to the 1600 cm^{-1} peak appeared to decrease with increased hydrocracking severity.

PYRROLIC COMPOUNDS

Anion Resin Exchange Eluates

Peaks at 3465 cm^{-1} are attributed to these compounds (Fig. 5) (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 appeared in the AI fractions of the feed and less severely hydrocracked samples as well as in asphaltenes. With increasing severity, more appeared in the AII fractions.

Neutral Fractions (Cyclohexane Eluates)

Small amounts of these compounds were present in the cyclohexane eluate indicating they were neither sufficiently acidic nor basic to be retained by either of the ion exchange resins (Fig. 5). These compounds may thus be indoles in which the pyrrolic function is highly hindered.

Cation Resin Exchange Fractions

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

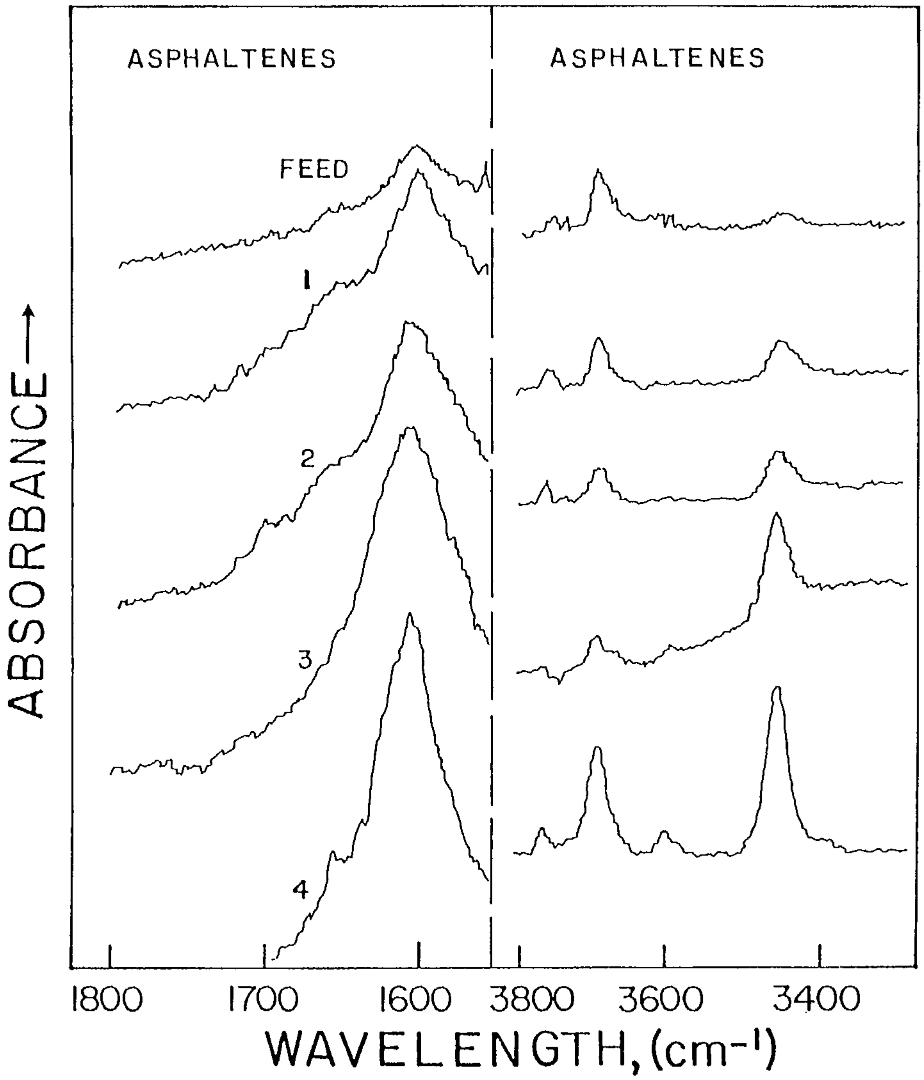

Fig. 4 - Infrared spectra of asphaltenes

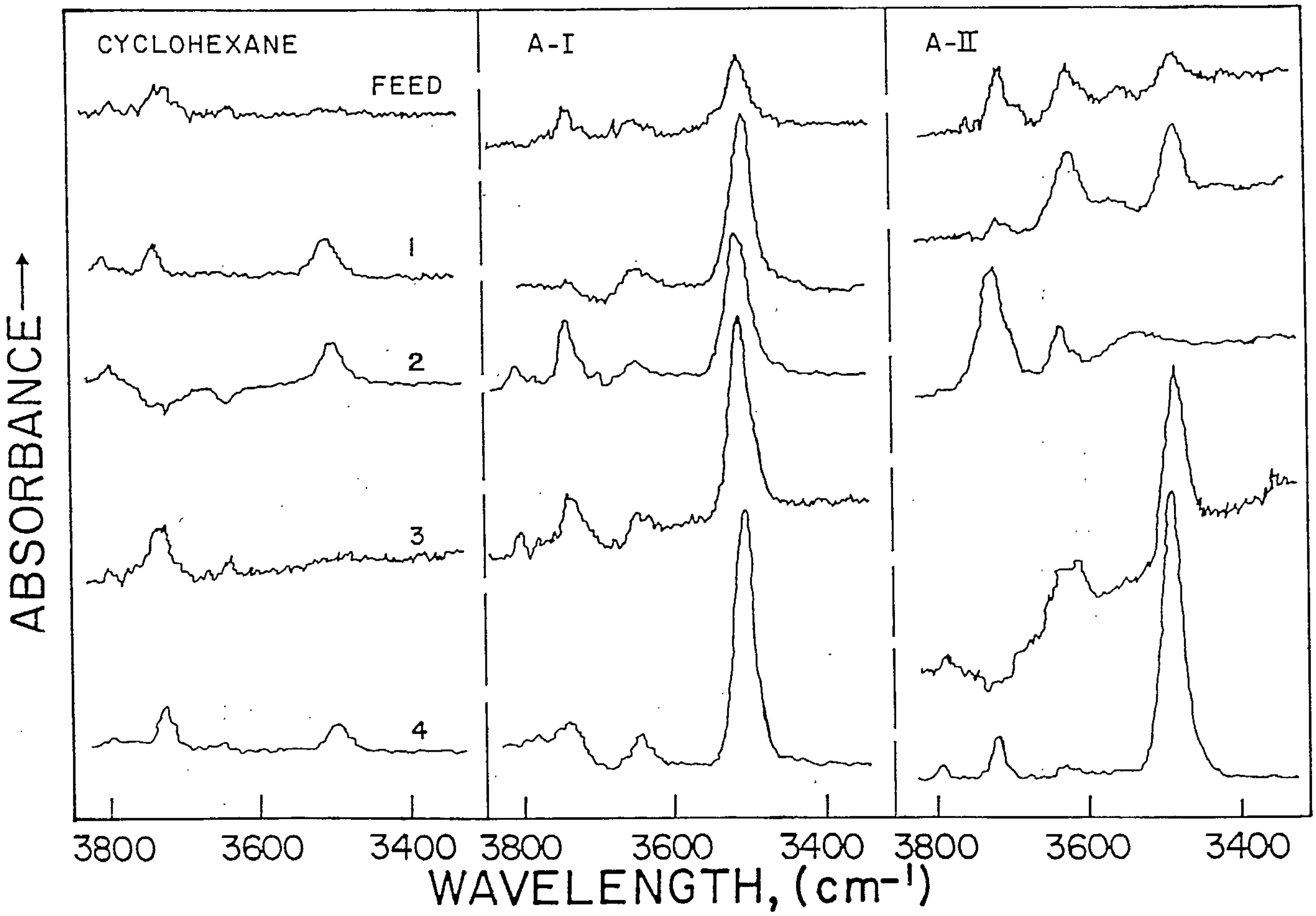

Fig. 5 - Infrared spectra of anion eluates

Table 5 - Milliequivalents of pyrrolic compounds in 100 g of bitumen and hydrocracked products

	Meq/pyrrolic compound/100 g				
Product	Feed	1	2	3	4
Pitch conversion (wt %)	-	26.0	49.0	79.0	89.0
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

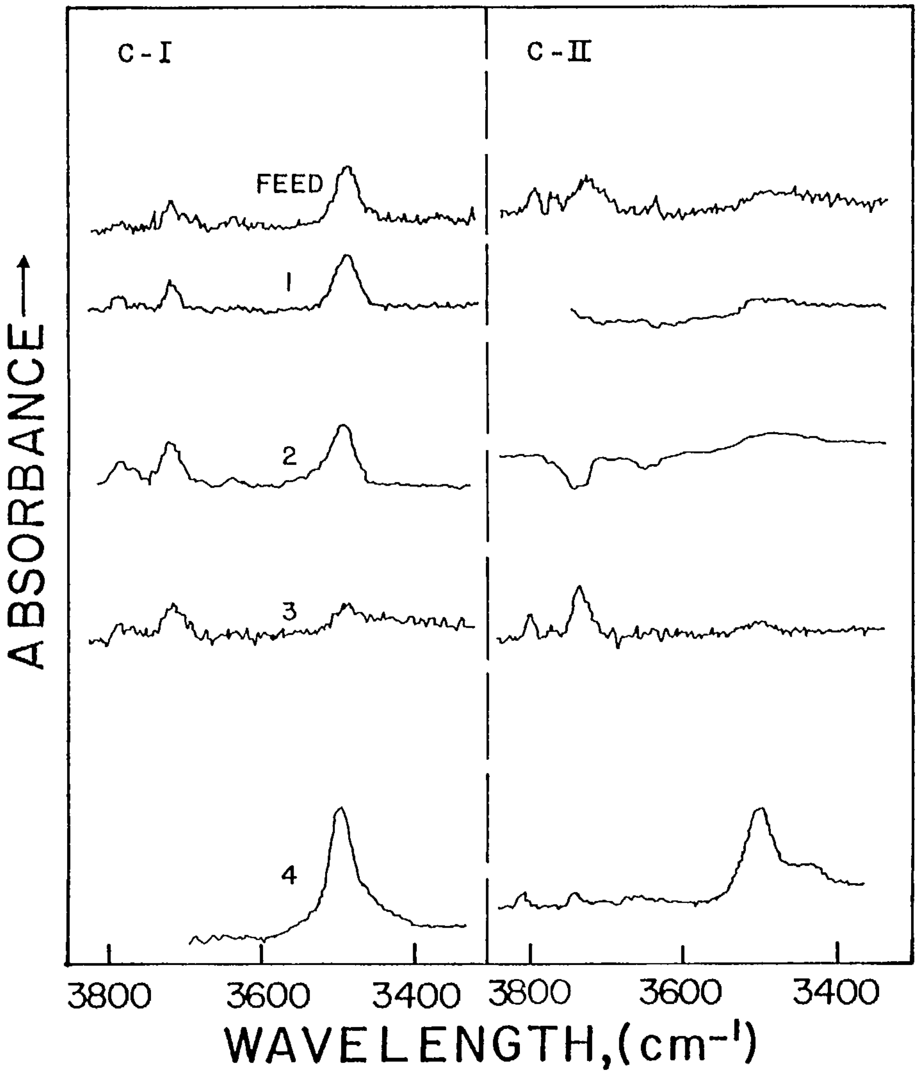

Fig. 6 - Infrared spectra of cation eluates

Asphaltenes

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

DETERMINING BASICITY BY TITRATION

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

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 increasing hydrocracking severities. Pyrrolic compounds increase but the 2-quinolones present in the bitumen degrade to traces in the highly-cracked product.

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REFERENCES

1. Merrill, W.H., Logie, R.B., and Denis, J.M. "A pilot scale investigation of thermal hydrocracking of Athabasca bitumen", Research Report R 281; Mines Branch [since renamed Canada Centre for Mineral and Energy Technology (CANMET)], Department of Energy, Mines and Resources; Dec. 1973.

2. Sawatzky, H., Ahmed, S.M., George, A.E., and Smiley, G.T. "Separation of nitrogenous and associated polar materials from bitumen and heavy oils". Preprints, Div Pet Chem, Inc., Am Chem Soc 11-20; Anaheim, CA; March 12-17, 1978.

3. Jewell, D.M., Weber, J.H., Bunger, J.W., Plancher, H., and Latham, D.R. "Ion-exchange, coordination, and adsorption chromatographic separation of heavy-end petroleum distillates". Anal Chem 44:8: 1391-1395; 1972.

4. McKay, J.F., Jewell, D.M., and Latham, D.R. "The separation of acidic compound types isolated from high-boiling petroleum distillates"; Sep Sci 7:361-370; 1972.

5. McKay, J.F., Cogswell, T.E., and Latham, D.R. "Analysis of acids in high-boiling petroleum distillates"; Fuel 54:50-61; 1975.

6. Bunger, J.W. "Characterization of a Utah tar sand bitumen"; In: Shale oil, tar sands, and related fuel sources; edited by T.F. Yen; Am Chem Soc 121-136; 1976.

7. McKay, J.F., Amend, P.J., Cogswell, T.E., Hamesberger, P.M., Erickson, R.B. and Latham, D.R. "Petroleum asphaltenes chemistry and composition"; Preprints Div Pet Chem, Inc., Am Chem Soc 708-715; New Orleans, LA, March 20-25, 1977.

8. McKay, J.F., Weber, J.H., and Latham, D.R. "Characterization of nitrogen bases in high-boiling petroleum distillates"; Anal Chem 48:6:891-898; 1976.

9. Pruden, B.B. and Denis, J.M. "Pilot plant thermal and catalytic treatment of heavy oils and bitumen"; ERP/ERL 77-22(J); CANMET, Energy, Mines and Resources Canada; 1977.

10. Wimer, D.C. "Potentiometric determination of amides in acetic anhydride"; Anal Chem 30:1:77-80; 1958.

11. Fritz, J.S. "Differential titration of amines"; Anal Chem 25:3:407-411; 1953.

12. Buell, B.E. "Nonaqueous, differential titration applied to a classification of basic and very weak basic nitrogen compounds in petroleum"; Anal Chem 39:7:756-761; 1967.

13. Bunger, J.W. "Techniques of analysis of tar sand bitumens"; Preprints, Div Pet Chem, Inc., Am Chem Soc 716-726; New Orleans, LA, March 20, 1977.

14. Hurd, C.D. "The pyrolysis of carbon compounds"; Am Chem Soc Monograph Series 236-269; The Chemical Catalog Company, New York; 1929.

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