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INVESTIGATION OF HYDROCARBON AND NITROGENOUS COMPOUND TYPES IN THREE CANADIAN PITCHES

A.E.George, R.Lega and M.A.Poirier

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PREFACE

The work on chemical characterization of pitch was conducted by Sandwell Beak Research Group (SBRG) under a contract for Energy Mines and Resources Canada (EMR) fully funded by Department of Supply and Services (DSS), over a period of six months starting first of August, 1980.

The work was conducted in SBRGs new research facilities in Toronto by Gabriela Teodosiu and Roxana Lega.

The scientific authority for the study was Dr. A. George of EMR.

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INTRODUCTION

This project is part of a series of studies on the upgrading of residual oil fractions into low sulphur distillates and fuel oils, and also dealing with economic uses for these types of products.

The importance of these studies in the present context of world economy and energy resides in the profitable and complete utilization of all fractions produced in refineries, be it from conventional or heavy oils or bitumen.

Unless it is upgraded to lower distillates the pitch fraction has a somewhat limited value - only a few markets being open for it; for example:

- heat and power production
- building and road construction
- additives in the production of coke briquettes

Even these uses are limited, by regulations limiting the sulphur and metals (V, Ni, Fe) content in the heavy fuel.

The so called "classic" methods of handling low grade residuals - as coking, visbreaking and delayed-coking are alternatives becoming less and less attractive, hence new processes are being developed such as hydrocracking, flexicoking, co-processing. These processes involve catalysts and/or severe hydrogenation.

The chemical properties of the pitch dictate the behaviour of this fraction during upgrading, in terms of yields and quality of products as well as operational problems - connected to coke formation, catalyst poisoning, severity of treatment (pressure, temperature, retention time, pumping characteristics, heating rates A.S.O.).

Viscosity, solubility and filtration characteristics depend almost exclusively upon the heteroatoms and the types of hydrogen bonding within the molecule.

Implicitly the type of reactor and/or fractionation procedure after upgrading are influenced by the chemical composition of the feedstock.

Pumping and combustion characteristics of the final products are connected to fluidity, low sulphur and nitrogen emissions and absence of trace metals.

Hydrogen consumption - economic factor - is significantly higher for larger polar molecules, and also increases with the oxygen content.

The objective of this project was a comparative characterization of three pitch samples (pitch, defined as vacuum bottoms distilling above 524° C, from Athabasca and Cold Lake bitumen and Lloydminster heavy oil).

The pitch samples were provided by EMR; no specifics regarding preparation or further use were supplied.

The correlation of chemical properties with conversion products and response to upgrading parameters was not part of this contract due to the confidential character of the study.

SUMMARY

The overall objective of this study was to provide a comparative study of chemical characteristics of three pitch samples. Pitch was defined as distillation residue above 525° C. The samples, two of which were obtained from bitumen distillations: Athabasca and Cold Lake, and the third from heavy oil distillation: Lloydminster were supplied by EMR.

The following outlines the work program undertaken:

1. The pitch samples as received were subjected to a complete analysis including: determination of elemental composition, ash, analysis of metals present in ash, molecular weight distribution and infrared analysis (IR).

2. Each pitch sample was fractionated in maltene and asphaltene fractions by extraction with three solvents: n-pentane, n-heptane and n-decane. The purpose was to provide information relevant to performance of the three solvents with respect to asphaltene solvation, in addition to the information on distillation of maltene versus asphaltene content in the pitches.

   The asphaltene fractions obtained from n-decane, n-heptane and n-pentane were quantified and subjected to the following analyses:

   - elemental composition (C,H,N,S)
   - molecular weight profile determination by Gel Permeation Chromatography
   - infrared spectra

   The maltene fractions were analysed in a similar way and the maltene fractions obtained with n-pentane from each pitch were further separated using liquid chromatography methods into: three acid fractions, three base fractions, a fraction containing neutral nitrogen compounds and a hydrocarbon fraction which was further fractionated into: saturate, monoaromatic, diaromatic and polyaromatic and polar hydrocarbon fractions.

   Elemental (C,H,O,S,N), atomic ratio H/C and average molecular weight were determined for each sub-fraction.

   Functional group analysis by IR was performed on each acid, base and neutral nitrogen fraction. Quantitative determination of aromatic, paraffinic and naphthenic carbon content was done on the saturates, monoaromatics, diaromatics and polyaromatics plus polars.

Discussion of Results

The Athabasca bitumen was the only pitch with a detectable ash content and this was analysed for metal content (V, Ni, Fe). Sulphur content was around 5.6% for all three pitches indicating the need for desulphurization prior to any upgrading process. The N content of 0.7% could lead to N poisoning of catalysts used in upgrading.

Of the three non-polar solvents used for the initial separation into maltenes and asphaltenes, n-pentane, the solvent with the smallest molecule, gave the largest amount of asphaltene (39.5% to 36.7%).

Results obtained with n-heptane and n-decane were very similar and do not justify the use of n-decane for this purpose. The molecular weights of both fractions increased with the use of n-heptane and n-decane indicating the solublization by the higher molecular solvent of the lower end of asphaltene fraction into the maltene fraction.

The liquid chromatography methods applied for maltene separation proved to be adequate, good reproducibility and mass balances were obtained over all steps.

The results of the chromatographic separation of maltenes indicated a higher content (20% greater) of heteroatomic compounds of the acid and base type in the Athabasca pitch.

The polynuclear aromatic fraction was found to be predominant in all three pitches representing between 21.1% in Cold Lake and 33.6% in Lloydminster.

The molecular weight of the heteroatomic type fractions was considerably higher than that of the hydrocarbon fractions.

Elemental analysis of fractions indicated a concentration in nitrogen and oxygen compounds in acid and base fractions, sulphur was evenly distributed in the acid, base neutral nitrogen, diaromatic and polyaromatic polar fractions, with values in general over 3% weight.

The saturate and monoaromatic hydrocarbon are the only fractions with a very low sulphur content (less than 0.05%). For all three pitches the saturate and monoaromatic hydrocarbon fractions showed a reduced content of heteroatoms (O,N and S).

Major types of compounds identified by IR methods were found to be as follows: carboxylic acids, phenols, carbazoles and amides in the acid fractions; pyridine benzologs, amides and pyrrolic compounds in the base fractions and amides and pyrrolic compounds in the neutral nitrogen.

The hydrocarbon fractions were found to be of predominantly naphthenic character - with a strong paraffinic presence in the saturate, mono and diaromates.

About 20% of the carbons present in the polyaromatic-polar fraction were aromatic and 70-75% naphthenic. Only 4-8% of the carbons in this fraction were found to be of paraffinic nature.

EXPERIMENTAL WORK
FOR CHEMICAL CHARACTERIZATION
OF PITCH SAMPLES

EXPERIMENTAL WORK

GENERAL

The pitch samples were analysed and further separated in fractions according to the type of compounds contained. The schema of the pitch separation is presented in Figure 1.

The first step in characterization of the pitch was to separate the asphaltenes from the maltenes, which were further separated according to the types of compounds they contain by ion exchange chromatography, coordination chromatography and adsorption chromatography.

Two samples of each pitch were processed in parallel to check the reproducibility of information.

Mass balances were calculated over each step and eventual losses were indicated.

1.0 PROCEDURES

1.1 Precipitation of Asphaltene Fraction

The removal of asphaltenes was achieved by precipitation with non-polar solvents (n-pentane, n-heptane and n-decane).

The pitch sample (approx. 100 g) was dissolved under nitrogen in a minimum amount of benzene (x 50 ml). The sample was heated on a steam bath while mixing well. When the material was well mixed, the solution was removed from the steam bath and 2 000 ml of solvent (n-pentane, n-heptane or n-decane) were added while stirring vigorously.

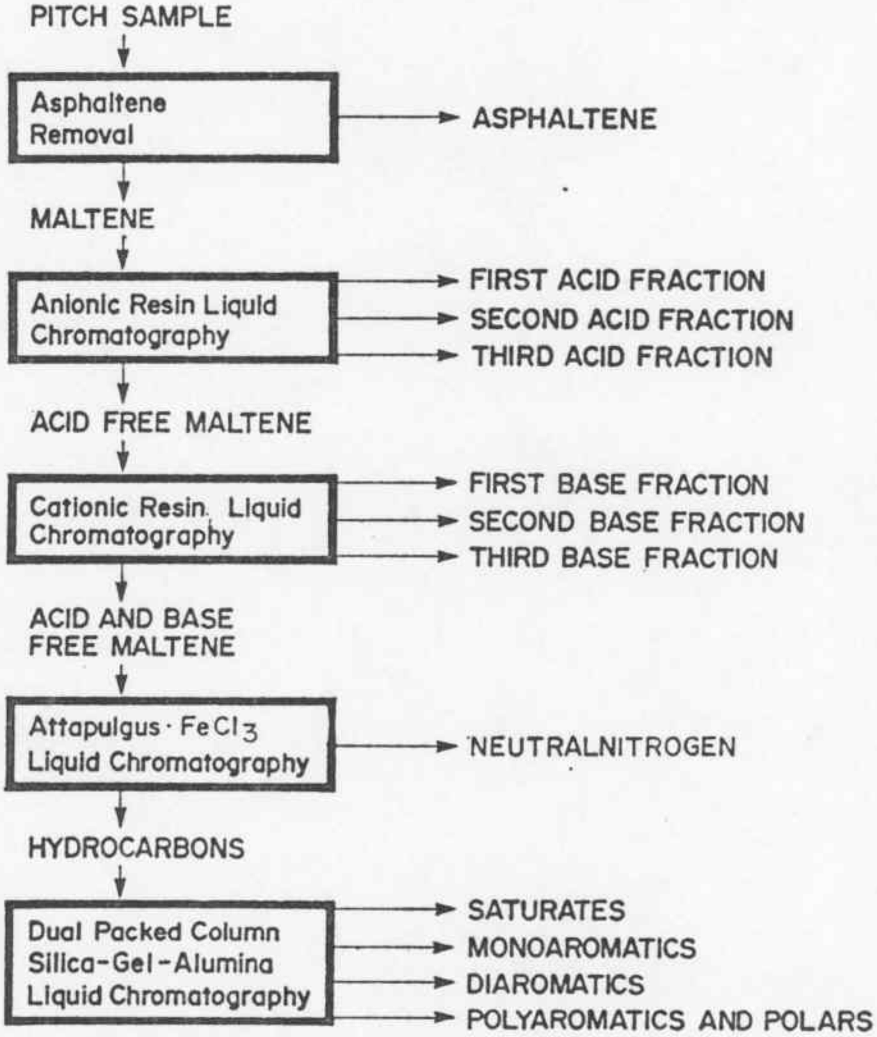
The mixture was allowed to stand covered for 12 hours. The asphaltene was separated by filtration, extracted with the same solvent in a Soxhlet extractor and dried in a vacuum oven. The dry sample was weighed and analysed. The main sample solubles and washings were combined and the solvent was completely evaporated from the maltene before the maltene fraction was weighed, analysed and used for further separations

1.2 Separation of Maltene Fractions by Liquid Chromatography

The maltene fraction was separated into fractions: acids, bases, neutral nitrogen compounds, saturated, monoaromatic and diaromatic hydrocarbons and a polyaromatic polar fraction.

SCHEMATIC OF THE PITCH FRACTIONATION

Figure I



1.2.1 Description of the Apparatus

Figure 2 illustrates the recycling chromatographic column used. All separations were carried out under nitrogen. Each column contained a recycling arrangement that permitted the continuous elution of the sample without the need of large quantities of solvent.

Two parallel samples from each pitch were used in order to check reproducibility. All fractions were freed of solvent by vacuum stripping, followed by a nitrogen gas sweep until a constant sample weight was obtained. Mass balances were calculated over each separation step.

1.2.2 Preparation of Resins and Adsorbents

Anion exhange resin - Amberlyst A-26 was washed four times with a methanolic HCl solution (10% volume aqueous HCl in methanol) and then rinsed with distilled water until neutral. The resin was activated with methanolic hydroxide solution (10% weight potassium hydroxide in methanol) and again washed with distilled water until neutral.

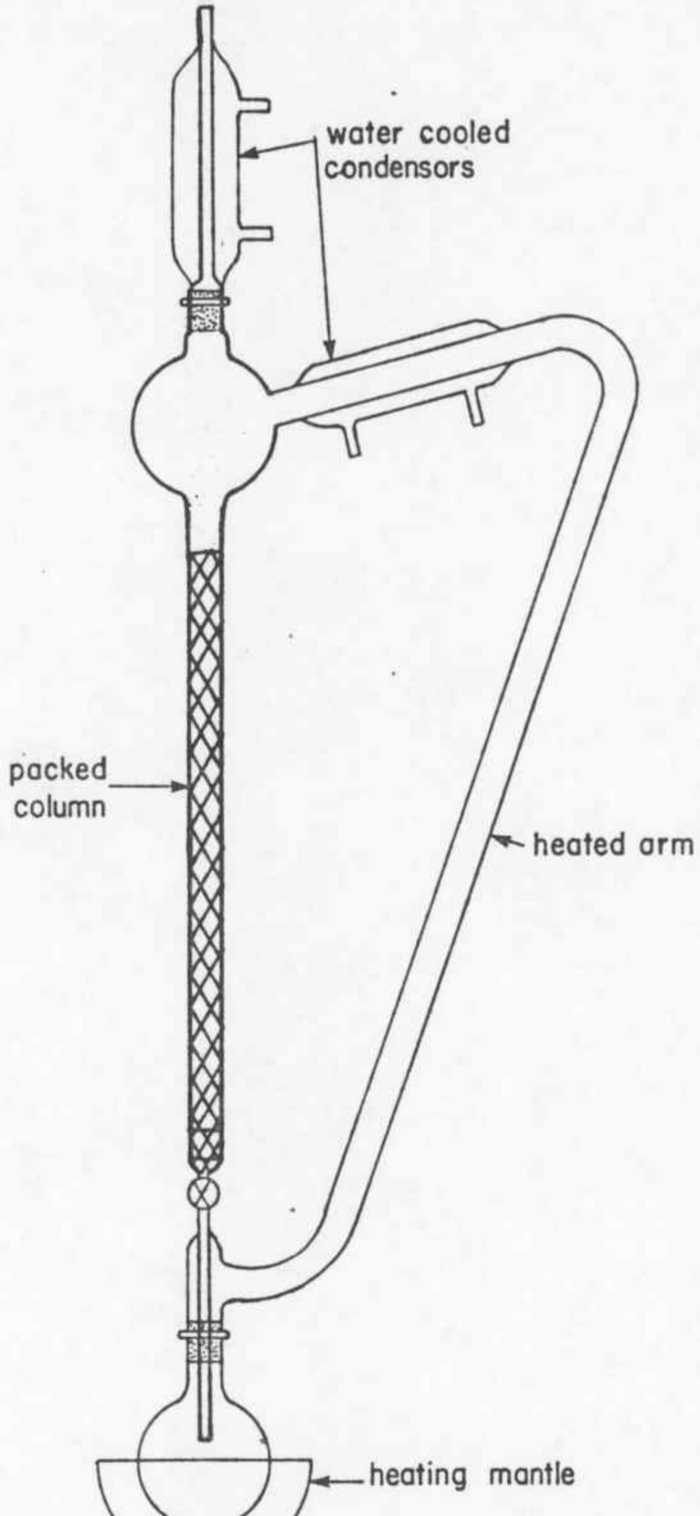
Final preparation of the resin was made by 24 hour Soxhlet extractions with each of the following solvents: methanol, benzene and pentane. The resin was then dried for 24 hours at 40° C in a vacuum oven before being packed into the separation columns.

Cation exchange resin - Amberlyst 15 was prepared by repeated washings with a methanolic hydroxide solution (10 weight percent potassium hydroxide in methanol) then rinsed and Soxhlet extracted with methanol. The resin was activated by adding it slowly to a stirred solution of 10 volume percent HCl in methanol. The resin was then washed with distilled water until the washings were neutral. Final preparation was made by 24 hour Soxhlet extraction of the resin with each of the following solvents: methanol, benzene, and pentane. The resin was then dried for 24 hours at 40° C in a vacuum oven.

Ferric Chloride on Attapulgus clay - Ferric chloride hexahydrate (10 weight percent ferric chloride hexahydrate in methanol) was contacted with Attapulgus clay (LVM, 50/80 mesh) for one hour. The ferric chloride - Attapulgus clay was filtered, washed several times with methanol, extracted with pentane for 48 hours in a Soxhlet extractor to remove non-adsorbed metallic salt, and dried at room temperature.

Schematic of the apparatus used for Liquid Chromatography

Figure 2



1.2.2 Preparation of Resins and Adsorbents

Adsorbent Silica-Alumina - The silica gel (70-230 mesh) was activated by heating 16 hours at 265° C.

Alumina gel (70-230 mesh) was activated by heating 16 hours at 400° C.

After activation, both adsorbents were stored in sealed containers until used in packed columns for hydrocarbon separation.

1.2.3 Separation of Acid Fractions

Fifty grams of anion exchange resin (Amberlyst A-26) was packed into each of the six columns (two for each of the three pitches). The sample, approximately 25 g of each deasphaltened pitch was dissolved in 200 cc of pentane and charged to the column.

Nonretained material was washed from the anionic resin with pentane for approximately 40 hours, using the recycling arrangement of the column shown in Figure 2.

After the acid free maltene fractions were removed, the reactive compounds (acids) were recovered in three sub-fractions by successive elution as follows: 16 hours with benzene, followed by 16 hours with 60% benzene - 40% methanol and 80% benzene-20% acetic acid. The three elution steps removed compounds of increasing acid strength.

The acid fractions separated this way were weighed after the complete solvent removal, and stored in sealed containers for analysis.

The acid free maltene fractions were subjected to further separation.

1.2.4 Separation of Base Fractions

The equipment used, amounts of resin and acid free sample, and procedure of introducing sample and eluting were the same as for the anion-exchange chromatography step.

The acid and base free fraction eluted with pentane was used for further separation, after solvent removal. The reactive material (basic) was removed from the resin by successive 16 hour elutions with benzene followed by 60% benzene-40% methanol, and finally with 55% benzene-37% methanol-8% isopropylamine.

1.2.5 Separation of Neutral Nitrogen Fraction

The acid, base free maltene fraction was further subjected to Ferric Chloride coordination chromatography for removal of neutral nitrogen compounds.

Approximately 50 g of Amberlyst A-26 anion-exchange resin were packed in the chromatography column. Then about 70 g of the ferric chloride-Attapulgus clay was packed on top of the resin. A 13 g sample of acid and base free deasphaltened pitch dissolved in pentane, was slowly percolat through the column. Entrained oil was removed by 40 hour pentane elution and subjected later to hydrocarbon separation. The neutral nitrogen compounds were desorbed from the complexed clay by 30 hours elution with 1.2-dichloroethane. The ferric chloride salt was retained on the resin and the nitrogen compounds were recovered in the eluate.

1.2.6 Separation of Hydrocarbon Fraction

The hydrocarbon fraction remaining after removal of acid, base and neutral nitrogen fractions is processed by adsorption chromatography on dual packed silica-alumina column for separation of saturate, mono, di and polyaromatic fractions. The adsorption column was a 3 cm diameter by 140 cm long glass tube. The bottom half of the column was packed with 250 g of fully activated alumina gel and the top half was packed with fully activated silica gel (175 g). About 4 g of sample were charged on each of the six columns. The four compound-type fractions could be collected at an approximate flow rate of 200 ml/hr with 2 500 ml of pentane for saturates, 3 000 ml of 5% benzene/95% n-pentane for mono-aromatics, 3 000 ml of 15% benzene/85% n-pentane for diaromatics, and 500 ml of 60% methanol/20% diethylether/20% benzene followed by 1 000 ml of methanol for polyaromatic-polar compounds.

General observations

It must be noted that the introduction of methanol on the columns (in particular anion exchange resin A-26) produced considerable swelling of the resin. The flow of the solvent through the column in some cases dropped to almost zero.

The product recovery from ferric chloride-Attapulgus clay was incomplete, 4% to 7% of the initial sample charged on the column was not recovered; it probably stayed on the column as it showed the change in the colour of the ferric chloride-Attapulgus clay at the end of elution with 1.2 dichloroethane apparatus.

1.3 Analysis of the Fractions

Infrared spectra were recorded on a Perkin Elmer using a 0.2 mm cell with a methylene chloride solvent for acid, base and neutral nitrogen fractions and on a Perkin Elmer 298 using a 1.0 mm KBr cell with carbon tetrachloride (spectro grade) and methylene chloride solvents for the hydrocarbon fractions.

Gel permeation chromatography was performed with a model ALC/GPC 24YC liquid chromatograph (Waters Associates, Miford, Mass.) equipped with a 440 Adsorbance detector and a differential refractometer R401.

All chromatograms were performed with a series of two μ Styragel columns (500^{o} A and 100^{o} A). The solvent was tetrahydrofuran at a flow rate of 1.3 ml/min. A 0.5% tetrahydrofuran solution of each sample was passed through a 0.5 μ filter prior to injection.

Two values for molecular weight were calculated from the GPC curves and presented in the tables: number average molecular weight, $\bar{M}n$, and weight average molecular weight, $\bar{M}w$ by the formulas

$$\bar{M}n = \frac{\sum_{i=1}^{N} hi}{\sum_{i=1}^{N} (hi/Mi)} \qquad \bar{M}w = \frac{\sum_{i=1}^{N} (hi\ Mi)}{\sum_{i=1}^{N} hi}$$

Where hi is the GPC curve height at the i^{th} volume increments and Mi - the molecular weight of the species eluted at the i^{th} retention volume. The equation assumes that hi is proportional to solute concentration and Mi is sampled in equal volume increments. The number average molecular weight ($\bar{M}n$) is frequently determined by one of the colligative property methods such as vapour-phase osmometry, boiling point elevation, freezing point depression and others.

The weight-average molecular weight, $\bar{M}w$, is normally determined from light-scattering measurements.

High molecular-weight species particularly influence the value of $\bar{M}w$, whereas the value obtained for $\bar{M}w$ is influenced more by species at the lower end of the molecular weight distribution.

Elemental analysis for carbon, hydrogen and nitrogen was carried out on a Perkin Elmer model 240 Elemental Analyzer. Carbon, hydrogen and nitrogen content were determined by analysis of the gases from the combustion of a sample with a thermal conductivity detector.

A LECO MODEL SC32 Sulphur Determinator measured sulphur content by infrared analysis of the gases from combustion of a sample. Oxygen was determined by difference.

The ash content was determined by volatilizing a sample with air to constant weight at 1 200° K.

Metal analysis was conducted by ashing 5 g of sample, dissolving the ash and determining the metal content instrumentally. Each solution of metals was analysed for lithium and vanadium by flame emission spectroscopy and for other metals by atomic adsorption spectroscopy.

2.0 RESULTS AND DISCUSSION OF DATA OBTAINED

2.1 Analysis of Pitch Samples

The pitch samples as received from EMR were analysed for elemental composition, ash, metal content in the ash, benzene insoluble, and molecular weight by GPC, before being separated in fractions. The results obtained for the three pitches are shown in Table 1.

Similar molecular weights were displayed by all three pitches as indicated by both values $\bar{M}n$ and $\bar{M}w$.

It seems significant that the Athabasca pitch is the only one containing 2.9% benzene insoluble and 1.2% ash.

The elemental composition of the three samples analysed indicates similar sulphur contents 5.5 - 5.7% and nitrogen 0.6 - 0.7%. The oxygen content 1.5 - 1.7% for Cold Lake and Lloydminster and somewhat higher 2% for Athabasca were calculated by difference.

The high sulphur content (around 5.6%) indicates the need for desulphurization prior to upgrading step for all pitches. The N content of 0.7 is a potential problem due to N poisoning of catalysts.

2.2 Precipitation of Asphaltene Fractions

The pitch samples were first subjected to a separation in maltene and asphaltene fractions using three solvents: n-pentane, n-heptane and n-decane. The asphaltene and maltene fractions were analysed for elemental composition and molecular weight. The results are presented in Table 2.

The amount of material precipitated depends on the ratio of polar to non-polar compounds in the solution and on the ratio of low molecular weight to high molecular weight compounds. The amount of asphaltene precipitated will depend entirely on how much the delicate balance of the solution is upset by the addition of a particular solvent.

From the three non-polar solvents used, the solvent with the smallest molecule gave the largest amount of asphaltene. The asphaltene content which was 39.5% for Athabasca, 38.9% for Cold Lake and 36.7% for Lloydminster when n-pentane was used, decreased to 22.6%, 22.1% and 22.6% respectively using n-heptane and further to 21.6%, 20.6% and 22.6% when n-decane was used.

Table 1 ANALYSIS OF INITIAL PITCH SAMPLES

TYPE OF PITCH	$\bar{M}n$ 1)	$\bar{M}w$ 2)	ELEMENTAL COMPOSITION (% WT)					ASH	BENZENE INSOL. % W	METAL ppm CONTENT		
			C	H	N	S	O			V	Fe	Ni
ATHABASCA	785	2889	81.3	9.3	0.7	5.5	2.0	1.2	2.9	330	789	260
COLD LAKE	805	2790	82.4	9.4	0.7	5.7	1.7	0	0	–	–	–
LLOYDMINSTER	865	2933	83.0	9.5	0.6	5.5	1.4	0	0	–	–	–

1) $$\bar{M}n = \frac{\sum_{i=1}^{N} hi}{\sum_{i=1}^{N} (hi/Mi)}$$

2) $$\bar{M}w = \frac{\sum_{i=1}^{N} (hi\ Mi)}{\sum_{i=1}^{N} hi}$$

Where hi is the GPC curve height at the i^{th} volume increment and Mi is the molecular weight of the species eluted at the i^{th} retention volume.

Table 2 ASPHALTENE PRECIPITATION COMPARATIVE RESULTS WHEN PENTANE, HEPTANE AND DECANE ARE USED FOR PRECIPITATION

SOLVENT USED	TYPE OF PITCH	FRACTION	% WT	$\bar{M}w^*$	$\bar{M}n^*$	ELEMENTAL COMPOSITION (% WT)				
						C	H	N	S	O
PENTANE	Athabasca	Maltene	60.5	1019	619	82.2	10.5	0.4	4.4	2.5
		Asphaltene	39.5	3438	929	81.9	8.4	1.3	7.4	1.0
	Cold Lake	Maltene	61.1	1026	640	82.5	10.5	0.6	4.7	1.7
		Asphaltene	38.9	3821	1010/ 893	81.8	8.2	1.1	7.5	1.4
	Lloydminster	Maltene	63.3	1140	667	82.7	10.7	0.3	4.5	1.8
		Asphaltene	36.7	4016	1129	82.3	8.1	1.2	7.3	1.1
HEPTANE	Athabasca	Maltene	77.4	1332	661	83.6	10.1	0.6	5.3	0.4
		Asphaltene	22.6	5392	1108	77.6	7.3	1.2	7.8	6.0
	Cold Lake	Maltene	77.9	1201	690	83.7	10.2	0.6	5.3	0.1
		Asphaltene	22.1	5442	1136	74.2	7.6	1.2	8.0	9.0
	Lloydminster	Maltene	77.4	1364	727	83.4	10.3	0.4	5.0	0.9
		Asphaltene	22.6	5684	1321	78.0	7.7	1.3	8.0	5.0
DECANE	Athabasca	Maltene	78.4	1408	694	83.7	10.0	0.6	5.8	0
		Asphaltene	21.6	7780	1108	79.7	7.8	3.5	8.4	0.6
	Cold Lake	Maltene	79.4	1187	727	83.5	10.1	0.5	5.9	0
		Asphaltene	20.6	3558	1321	76.8	7.4	4.0	8.7	3.1
	Lloydminster	Maltene	77.4	1303	690	83.5	10.1	0.5	5.6	0
		Asphaltene	22.6	6586	1194	76.1	7.2	3.2	8.1	5.4

* $\bar{M}n$ and $\bar{M}w$ - see Table 1

When a non-polar solvent is added, the ratio of polar and non-polar molecule in the sample is altered and the polar molecules form H-bonded aggregates and precipitate as asphaltene.

The use of n-heptane versus n-pentane can increase the amount of maltene, but the use of n-decane over n-heptane did not bring a significant change and in view of the difficulty of solvent removal due to its high boiling point the use of n-decane does not appear to be justified.

Asphaltene will include the most polar and the highest molecular weight species present in the complex mixture.

This can be easily be seen from the distribution of heteroatoms and molecular weight between asphaltene and maltene fractions - Table 2.

The molecular weights of maltene fractions are several times lower than molecular weight of asphaltene fractions and depend on the solvent used. The molecular weight of the asphaltene fractions of Athabasca pitch increased from $\bar{M}w$ 3438 when n-pentane was used to value $\bar{M}w$ 5392 using n-heptane and $\bar{M}w$ 7780 for n-decane.

The elemental composition of fractions obtained from the three pitches is very similar and this aspect does not change with the solvent used.

The asphaltenes have a hydrogen content lower than maltenes. The atomic H/C ratio for maltene is between 1.4 - 1.5 compared to 1.15 - 1.23 for asphaltenes. Nitrogen and sulphur content are higher in asphaltene as it should be expected.

2.3 Maltene Fraction Separation

The results of the chromatographic fractionation of the three pitches are presented in Table 3. Two parallel samples of pitch were processed according to the procedure discussed. The mass balances over each step of separation were 98% or better with the exception of the neutral nitrogen step where 4-9% of the sample charged remained adsorbed on the column after the dichloroethane elution. The results obtained from fractionation indicate differences in the concentration of various fractions in the three pitches.

The Athabasca pitch has a slightly higher total acid fractions content (4.9 as opposed to 3.9 and 3.4) and a higher basic fractions content (5.7 compared to 4.9 and 5.0).

Table 3 CHEMICAL COMPOSITION OF THREE PITCH SAMPLES

TYPE OF PITCH FRACTION SEPARATED	ATHABASCA		COLD LAKE		LLOYDMINSTER	
	% WT	$\bar{M}w$	% WT	$\bar{M}w$	% WT	$\bar{M}w$
ASPHALTENE*	39.5	3438	38.9	3821	36.7	4016
ACID FRACTION I	0.8	1422	0.6	1779	0.5	1679
FRACTION II	1.4	1732	1.2	1118	0.9	1152
FRACTION III	2.7	3194	2.2	2037	1.9	2320
BASE FRACTION I	2.5	1360	1.6	1799	1.5	1802
FRACTION II	1.2	1447	1.1	1437	1.0	1470
FRACTION III	2.0	1786	2.2	1612	2.5	1515
NEUTRAL NITROGEN	7.5	1900	7.1	1968	8.7	2113
SATURATES	5.1	664	8.3	730	5.9	731
MONOAROMATICS	3.2	738	5.6	733	3.6	810
DIAROMATICS	1.0	741	7.6	691	1.0	786
POLYNUCLEAR & POLAR	30.0	681	21.1	794	33.6	796
TOTAL RECUPERATED	96.9		97.5		97.8	

* precipitated with pentane

The acid Fraction III containing the strongest (most readily hydrogen bondable) acids is more than half of the total acid fraction for all three pitches.

The neutral nitrogen content is 8.7% for Lloydminster and 7.5% and 7.1% respectively for Athabasca and Cold Lake.

The polynuclear-polar fraction is the predominant fraction for the three pitches; it represents 30% weight for Athabasca, 21.1% for Cold Lake and 33.6% for Lloydminster.

The hydrocarbon content (saturates + monoaromatics + diaromatics) is only 9.3% weight and 10.5% weight for Athabasca and Lloydminster but it reaches the value of 21.5% weight for Cold Lake.

The Athabasca pitch is richer in total acidic and base material (10.8% weight) than Cold Lake and Lloydminster (8.9% and 8.3% respectively).

When it comes to hydrocarbons, Cold Lake has a higher saturate, monoaromatic and diaromatic content, but a much lower polynuclear and polar fraction.

The weight average molecular weight $\bar{M}w$ presented in the same Table 3 shows unusually high values for Acid Fr. III and neutral nitrogen fraction. This could be explained by the presence of intermolecular associations.

The hydrocarbon fractions with a reduced content of heteroatoms show molecular weights well below 1 000, while the $\bar{M}w$ varies between 1 200-3 200 for the acid fractions, 1 300-1 800 for the base fractions and it was around 2 000 for the neutral nitrogen fractions. Elemental analyses of acid, base, neutral N and hydrocarbon fractions are presented in Table 4,5,6 and 7 and in Figures 3 and 4 for easy comparison.

Nitrogen and oxygen compounds are concentrated in the acid and base fractions. The nitrogen doesn't appear to concentrate in any particular acid fraction and varies between 1.5% - 0.7% for Athabasca; 1.0% - 0.8% for Cold Lake and 1.1% - 0.7% for Lloydminster. The base fractions have a higher nitrogen content, increasing with the basicity of the fractions. The nitrogen content in base fraction III is 3.6% in Lloydminster and 1.8% for Athabasca and Cold Lake. The neutral nitrogen fractions are lower in nitrogen than the base fraction III. The highest value is 1.66% weight in Athabasca. Cold Lake and Lloydminster were 0.9% weight and 1.0% weight respectively.

Table 4 ELEMENTAL COMPOSITION OF ACID FRACTIONS

TYPE OF PITCH	FRACTION	ELEMENTAL COMPOSITION (% WT)							
		C	H	N	S	O	$\bar{M}n$ 1)	$\bar{M}w$ 2)	H/C
ATHABASCA	Oil charged	82.2	10.5	0.4	4.4	2.5	619	1019	1.53
	C_5 eluate	83.7	10.2	0.8	5.3	0.0	636	1101	1.46
	C_6H_6 eluate	83.6	9.5	1.0	4.9	1.0	712	1422	1.36
	C_6H_6-MeOH eluate	80.9	9.3	1.5	4.0	4.3	799	1732	1.38
	C_6H_6-AcOH eluate	75.6	9.9	0.7	3.3	10.5	848	3194	1.57
COLD LAKE	Oil charged	82.5	10.5	0.6	4.8	1.6	640	1026	1.53
	C_5 eluate	84.0	10.4	0.5	5.1	0.0	669	1124	1.49
	C_6H_6 eluate	82.5	9.6	1.0	5.0	1.9	784	1779	1.39
	C_6H_6-MeOH eluate	80.6	9.2	0.8	3.6	5.8	664	1118	1.36
	C_6H_6-AcOH eluate	55.2	7.2	0.9	1.7	35.0	812	2037	1.56
LLOYDMINSTER	Oil charged	82.7	10.7	0.3	4.5	1.8	667	1140	1.55
	C_5 eluate	83.5	10.9	0.3	5.0	0.3	657	1032	1.57
	C_6H_6 eluate	77.9	9.4	0.9	4.5	7.3	842	1679	1.44
	C_6H_6-MeOH eluate	81.0	9.4	0.7	4.4	4.5	696	1152	1.39
	C_6H_6-AcOH eluate	58.0	7.2	1.1	1.8	31.9	907	2320	1.49

1), 2) - see Table 1

Table 5 ELEMENTAL COMPOSITION OF BASIC FRACTIONS

TYPE OF PITCH	FRACTION	ELEMENTAL COMPOSITION (% WT)							
		C	H	N	S	O	$\bar{M}_n$ 1)	$\bar{M}_w$ 2)	H/C
ATHABASCA	Acid free oil charged	83.7	10.2	0.8	5.3	0.0	636	1101	1.46
	Pentane eluate	84.1	10.8	0.5	4.5	0.1	587	1004	1.54
	Benzene eluate	81.5	9.5	1.2	6.4	1.4	639	1360	1.40
	Benzene-MeOH eluate	82.5	9.8	1.6	4.8	1.3	735	1447	1.42
	Benzene-MeOH-IPA eluate	83.1	10.0	1.8	4.2	0.9	797	1786	1.44
COLD LAKE	Acid free oil charged	84.0	10.4	0.5	5.1	0.0	669	1124	1.49
	Pentane eluate	84.1	10.3	0.5	5.1	0.0	627	1070	1.47
	Benzene eluate	79.9	9.8	1.4	5.0	3.9	847	1799	1.47
	Benzene-MeOH eluate	79.9	9.9	1.1	3.5	5.6	750	1437	1.49
	Benzene-MeOH-IPA eluate	79.2	9.3	1.8	4.3	5.4	717	1612	1.41
LLOYDMINSTER	Acid free oil charged	83.5	10.9	0.3	5.0	0.3	657	1032	1.57
	Pentane eluate	84.1	10.4	0.5	5.0	0.0	641	1106	1.48
	Benzene eluate	80.0	9.6	0.93	5.27	4.2	886	1802	1.44
	Benzene-MeOH eluate	81.9	9.8	1.8	2.9	3.6	815	1470	1.44
	Benzene-MeOH-IPA eluate	82.3	9.6	3.6	4.1	0.4	820	1515	1.40

1), 2) - see Table 1

Table 6 ELEMENTAL COMPOSITION OF NEUTRAL NITROGEN FRACTION

TYPE OF PITCH	FRACTION	ELEMENTAL COMPOSITION (% WT)							
		C	H	N	S	O	$\bar{M}_n$ 1)	$\bar{M}_w$ 2)	H/C
ATHABASCA	Oil charged	84.1	10.8	0.5	4.5	0.1	584	1004	1.54
	Pentane eluate	84.7	10.8	0.5	4.0	0.0	670	1073	1.53
	Neutral Nitrogen *	82.3	9.8	1.66	5.9	0.3	912	1900	1.43
COLD LAKE	Oil charged	84.1	10.3	0.5	5.1	0.0	627	1070	1.47
	Pentane eluate	84.1	11.0	0.3	4.6	0.0	593	817	1.57
	Neutral Nitrogen *	81.6	9.8	0.9	5.7	2.0	1020	1968	1.44
LLOYDMINSTER	Oil charged	84.1	10.4	0.5	5.0	0.0	641	1106	1.48
	Pentane eluate	84.6	10.7	0.3	4.4	0.0	642	886	1.52
	Neutral Nitrogen *	81.9	9.5	1.0	6.2	1.4	958	2113	1.39

* Dark brown solid
1), 2) - see Table 1

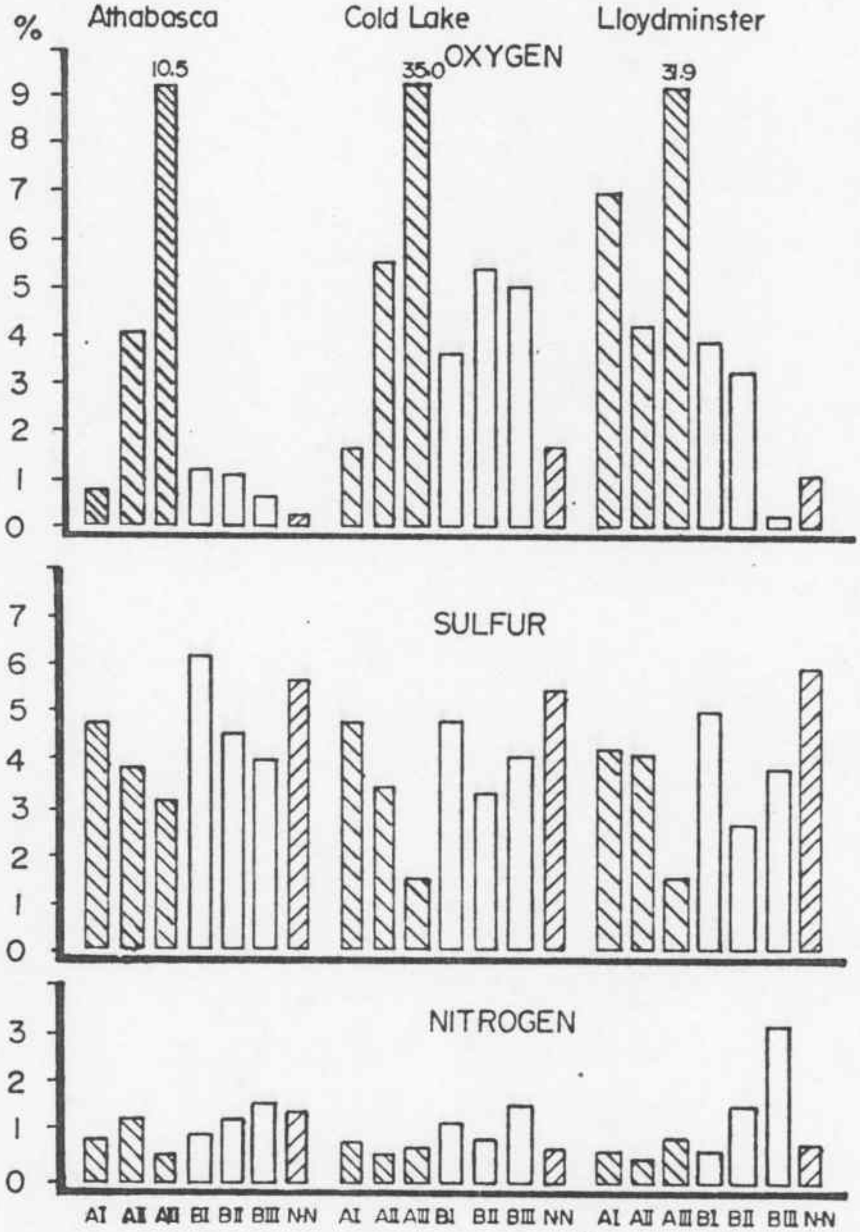
Table 7 ELEMENTAL COMPOSITION OF HYDROCARBON FRACTIONS

TYPE OF PITCH	FRACTION	ELEMENTAL COMPOSITION (% WT)							
		C	H	N	S	O	$\bar{M}_n$ 1)	$\bar{M}_w$ 2)	H/C
ATHABASCA	Acid, Base N_2 Neutral Free oil charged	84.7	10.8	0.5	4.0	0	670	1073	1.53
	Saturate	86.6	13.1	0.3	<0.05	0	563	664	1.82
	Monoaromatic	87.0	12.3	0.3	<0.05	0.4	590	738	1.70
	Diaromatic	84.9	10.5	0.5	4.1	0	536	741	1.48
	Polyaromatic,polar	83.5	9.6	0.5	5.9	0.5	495	681	1.38
COLD LAKE	Acid, Base N_2 Neutral Free oil charged	84.1	11.0	0.3	4.6	0	593	817	1.57
	Saturate	86.3	12.8	0.3	0.6	0	602	730	1.78
	Monoaromatic	86.2	12.0	0.3	0	1.5	572	733	1.67
	Diaromatic	84.4	10.2	0.3	4.9	0.2	524	691	1.45
	Polyaromatic,polar	81.9	9.3	0.7	5.9	2.2	540	794	1.36
LLOYDMINSTER	Acid, Base N_2 Neutral Free oil charged	84.9	10.4	0.3	4.4	0	642	886	1.47
	Saturate	86.5	13.3	0.2	<0.05	0	608	731	1.84
	Monoaromatic	87.2	12.6	0.2	<0.05	0	645	810	1.73
	Diaromatic	86.8	11.4	0.9	nes	0	589	786	1.58
	Polyaromatic,polar	82.3	9.6	0.8	5.8	1.4	547	796	1.40

1), 2) - see Table 1
nes - not enough sample

Heteroatom concentration in acid, base and neutral-nitrogen fractions

Figure 3



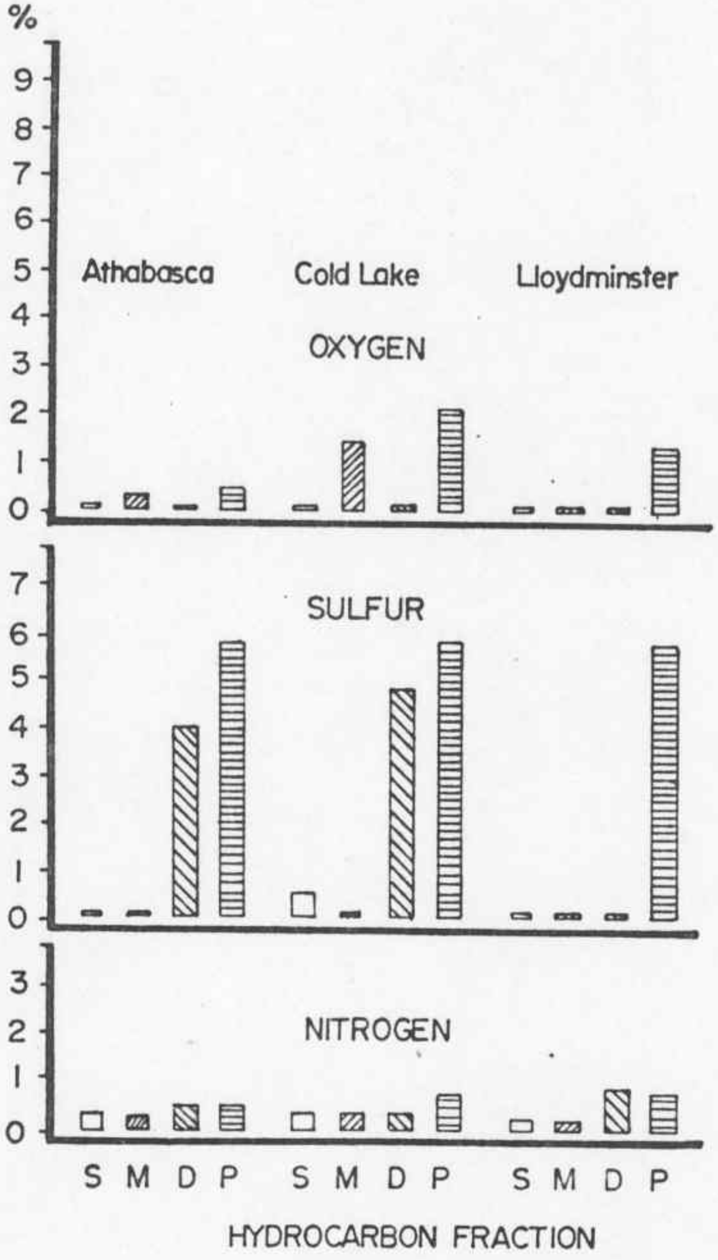
AI = Acid fraction I
AII = Acid fraction II
AIII = Acid fraction III

BI = Base fraction I
BII = Base fraction II
BIII = Base fraction III

N-N = Neutral-Nitrogen fraction

Heteroatom concentration in hydrocarbon fractions

Figure 4



S = Saturate Hydrocarbon
M = Monoaromatic Hydrocarbon
D = Diaromatic Hydrocarbon
P = Polyaromatic-Polar Fraction

Hydrocarbon fractions show low nitrogen content 0.2% - 0.3% for saturate and monoaromatic and slightly higher 0.5% - 0.9% for diaromatic and polyaromatic polar fractions. Lloydminster reaches the highest value of 0.9% weight.

Sulphur is rather evenly distributed in the acid, base, neutral nitrogen and diaromatic and polyaromatic-polar fractions, indicating that sulphur compounds have not been concentrated in any of the fractions. A somewhat lower sulphur content for Fraction III acid in Cold Lake, 1.7% Cold Lake and 1.8% Lloydminster was observed. The hydrocarbon saturate and monoaromatic are the only fractions with a very low sulphur content (less than 0.05%).

The values for oxygen (calculated by difference) do not present a consistent value. The trends in oxygen values are probably valid but the absolute percentages of oxygen reported shall not be used as absolute figures, since errors can be compounded due to method of calculation. High values for oxygen were found in all acid fractions, but especially in Fr. III - the fraction expected to contain carboxylic acid. Overall, the oxygen content found in base fractions is much lower than in the acid fractions, lower in the case of Athabasca pitch (1.4; 1.3; 0.9) higher in the case of Cold Lake (3.9; 5.6; 5.4). The hydrocarbon fractions have a very low content in oxygen, the presence of oxygen 1.7% weight and 2.0% weight in Lloydminster and Cold Lake polyaromatic polar fraction might be explained by the presence of furan type oxygen compounds that are not removed by the resin or the ferric chloride.

The H/C ratio found for acid fractions is in the range of 1.5 - 1.57 for the Fraction III while the other two fractions were around 1.4. All basic fractions have a H/C around 1.4 and it does not change from one pitch to another. Similar values were found for neutral nitrogen fractions H/C = 1.42 (Athabasca); 1.44 (Cold Lake) and 1.39 (Lloydminster). The H/C ratios for hydrocarbon fractions have high values (1.81 - Athabasca, 1.78 - Cold Lake and 1.84 - Lloydminster) for saturate fractions and lower values (1.38 - Athabasca, 1.36 - Cold Lake and 1.40 - Lloydminster) for polyaromatic polar fractions, indicating a high aromatic hydrocarbon content in these fractions.

Weight average molecular weight $\bar{M}w$ and number average molecular weight $\bar{M}n$ were calculated from gel permeation chromatography curves. Any average molecular weight value shall be regarded only as an average, it doesn't give an absolute value of molecular weight and we intend to use this value to compare the whole pitch with the different fractions obtained. The hydrocarbon fractions show consistently lower molecular weights than the non-hydrocarbon fractions, and indication that there is less intermolecular association in hydrocarbon fractions than in non-hydrocarbon fractions. $\bar{M}n$ of saturates monoaromatics, diaromatics and polyaromatics-polars, in that order, decrease from $\bar{M}n=563$ to $\bar{M}n=495$ for Athabasca; from $\bar{M}n=602$ to $\bar{M}n=540$ for Cold Lake and from $\bar{M}n=608$ to $\bar{M}n=547$ for Lloydminster. The $\bar{M}n$ values are higher in Acid Fraction III for all three pitches, due probably to molecular association, where as for base fractions the values don't show a tendency, they are around $\bar{M}n=700$ for Athabasca and Cold Lake and around $\bar{M}n=800$ for Lloydminster. The highest values were found for neutral nitrogen fractions, where $\bar{M}n$ ranged from 912 for Athabasca pitch; 1020 for Cold Lake and 958 for Lloydminster.

Average property data such as elemental analysis and average molecular weights can be used together to describe an average molecular composition in each fraction. In Table 8 following are presented tentative molecular formulas as calculated on this basis for each fraction. The estimates are for average molecules and may or may not be an accurate description of the molecules actually present, because the distribution of heteroatoms in individual molecules is not known.

Acids, bases and neutral nitrogen fractions were analysed by infrared spectroscopy in methylene chloride solutions. The partial infrared spectra are presented in Figures 5 to 9.

The spectra obtained for acid fractions are shown in Figures 5 and 6. The major types of compounds identified in acid fractions were carboxylic acids, phenols, carbazoles and amides.

The infrared spectra of Acid Fraction I for the three pitches had in common strong peaks at 3 585 cm-1 due to phenolic O-H stretching even stronger peaks at 3 460 cm^{-1} due to pyrrolic N-H stretching and three peaks between 1 600 and 1 700 cm^{-1} due to amide carbonyl compounds. The amide carbonyl peaks are more important for the Lloydminster pitch Acid Fraction I. The higher carbonyl and phenol absorption for Lloydminster Acid Fraction I might be correlated with high oxygen content found in this fraction 7.3% weight.

The infrared spectra of Acid Sub-fractions II showed the same absorption bands but with more phenolic absorption at 3 585 cm^{-1} and a second phenol absorption at 3 540 cm^{-1} (ascribed to phenols having intramolecularly Π-bonded hydroxyl groups) for Athabasca and Cold Lake pitches. The absorption at 3 585 cm^{-1} due to phenolic O-H stretching seems less important in Acid Fraction II than in Acid Fraction I for Lloydminster.

Table 8 Tentative Molecular Composition Representations (calculated)

Acid Fractions

	FrI	$C_{49.6}$	$H_{67.6}$	$N_{0.5}$	$S_{1.0}$	$O_{0.4}$
A	FrII	$C_{53.8}$	$H_{74.3}$	$N_{0.8}$	$S_{1.0}$	$O_{2.1}$
	FrIII	$C_{53.4}$	$H_{83.9}$	$N_{0.4}$	$S_{0.8}$	$O_{5.5}$
	FrI	$C_{53.9}$	$H_{75.2}$	$N_{0.5}$	$S_{1.2}$	$O_{0.9}$
CL	FrII	$C_{44.6}$	$H_{61.1}$	$N_{0.3}$	$S_{0.7}$	$O_{2.4}$
	FrIII	$C_{37.3}$	$H_{58.4}$	$N_{0.5}$	$S_{0.4}$	$O_{17.7}$
	FrI	$C_{54.6}$	$H_{79.1}$	$N_{0.5}$	$S_{1.1}$	$O_{3.8}$
LM	FrII	$C_{46.0}$	$H_{65.4}$	$N_{0.3}$	$S_{0.9}$	$O_{1.9}$
	FrIII	$C_{43.8}$	$H_{65.3}$	$N_{0.7}$	$S_{0.5}$	$O_{18.0}$

Base Fractions

	FrI	$C_{43.4}$	$H_{60.7}$	$N_{0.5}$	$S_{1.2}$	$O_{0.6}$
A	FrII	$C_{50.5}$	$H_{72.0}$	$N_{0.8}$	$S_{1.1}$	$O_{0.6}$
	FrIII	$C_{55.2}$	$H_{79.70}$	$N_{1.0}$	$S_{1.0}$	$O_{0.4}$
	FrI	$C_{56.4}$	$H_{83.0}$	$N_{0.8}$	$S_{1.3}$	$O_{2.0}$
CL	FrII	$C_{49.9}$	$H_{74.2}$	$N_{0.6}$	$S_{0.8}$	$O_{2.6}$
	FrIII	$C_{47.3}$	$H_{66.6}$	$N_{0.9}$	$S_{0.9}$	$O_{2.4}$
	FrI	$C_{59.0}$	$H_{85.0}$	$N_{0.6}$	$S_{1.4}$	$O_{2.3}$
LM	FrII	$C_{55.6}$	$H_{79.8}$	$N_{1.0}$	$S_{0.7}$	$O_{1.8}$
	FrIII	$C_{56.2}$	$H_{78.7}$	$N_{2.1}$	$S_{1.0}$	$O_{0.2}$

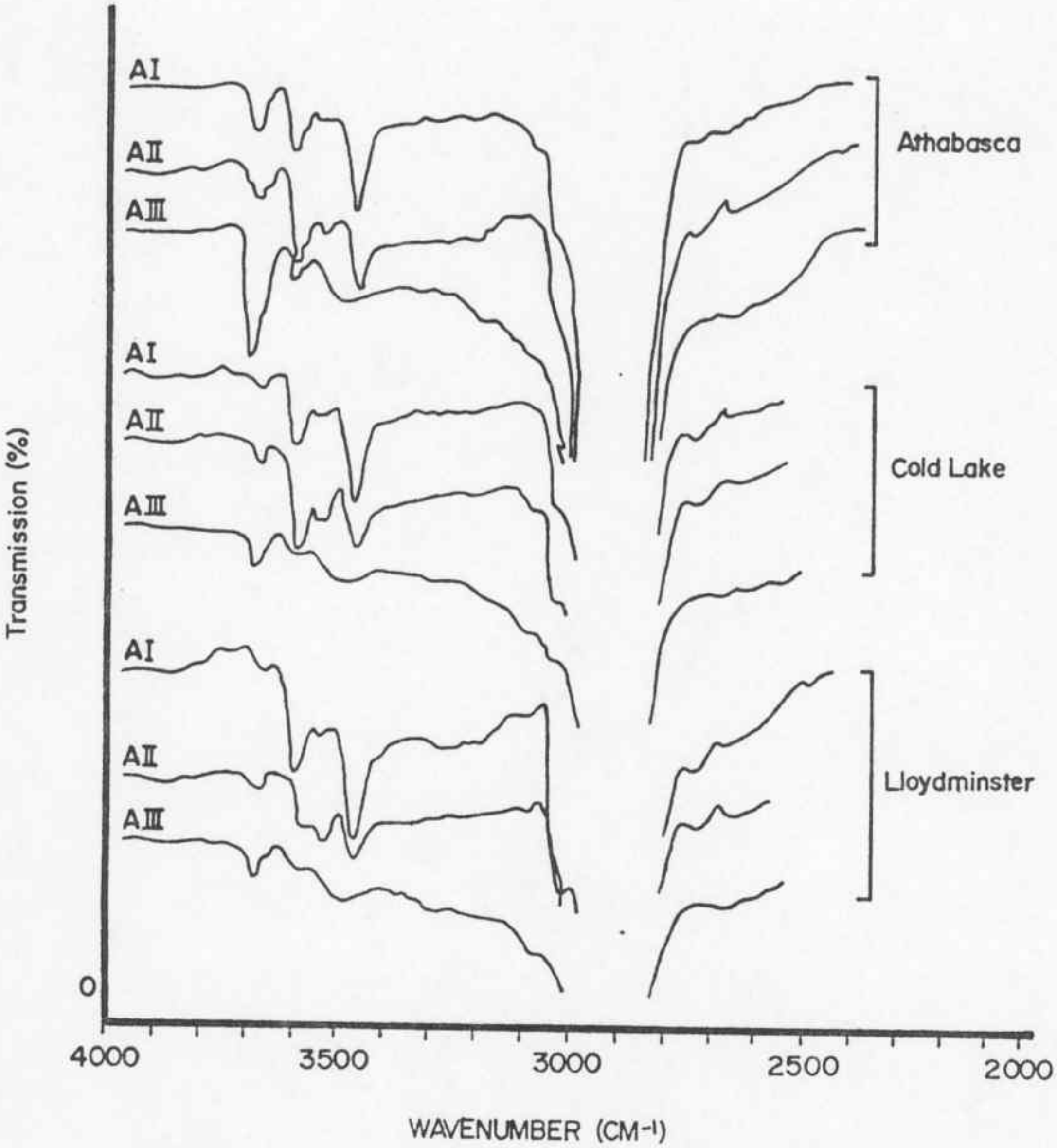
Table 8 (continued)

				Neutral Nitrogen Fractions		
A		C 62.5	H 89.3	N 1.0	S 1.6	O 0.1
CL		C 69.3	H 99.9	N 0.6	S 1.8	O 1.2
LM		C 65.3	H 91.0	N 0.6	S 1.8	O 0.8
				Hydrocarbon Fractions		
	Sat	C 40.6	H 73.7	N 0.1	S 0.0	O 0.
A	MA	C 42.7	H 72.5	N 0.1	S 0.0	O 0.1
	DA	C 37.9	H 56.3	N 0.2	S 0.7	O 0.
	PA-P	C 34.4	H 47.5	N 0.2	S 0.9	O 0.1
CL	Sat	C 43.3	H 77.0	N 0.1	S 0.1	O 0.
	MA	C 41.1	H 68.6	N 0.1	S 0.	O 0.5
	DA	C 36.8	H 53.4	N 0.1	S 0.8	O 0.0
	PA-P	C 36.8	H 50.2	N 0.3	S 1.0	O .07
LM	Sat	C 43.8	H 80.8	N 0.0	S 0.0	O 0.
	MA	C 46.8	H 81.2	N 0.0	S 0.0	O 0.
	DA	C 42.6	H 67.1	N 0.3	S nef	O 0.
	PA-P	C 37.5	H 52.5	N 0.3	S 1.0	O 0.5

Notes
A = Athabasca Bitumen Pitch
CL = Cold Lake Pitch
LM = Lloydminster Pitch
Sat = Saturate
MA = Monoaromatic
DA = Diaromatic
PA-P= Polyaromatic-Polar

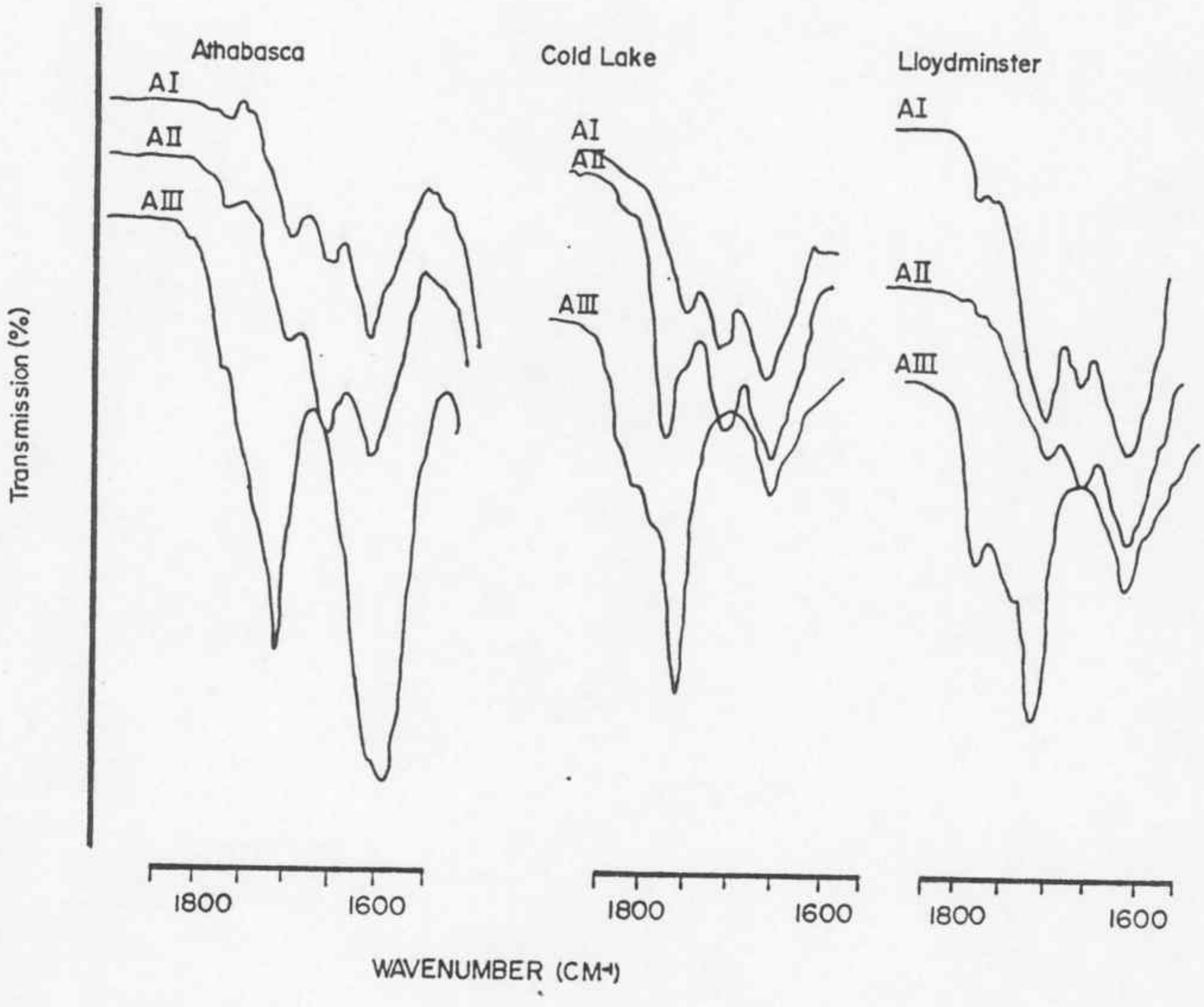
Infrared spectra of acid fractions

Figure 5



Infrared spectra of acid fractions

Figure 6



All three Acid Fraction II show less pyrrolic N-H absorption. Characteristics for Acid Fractions III are the strong absorption of carboxylic acid carbonyl monomer and dimer bands at 1 725 and 1 710 cm^{-1}. The pyrrolic N-H absorption at 3 460 cm^{-1} becomes a shoulder and for all three pitches the absorption of hydrogen bonded carboxylic acid and phenolic hydroxyl groups can be seen in the region 3 500 - 2 300 cm^{-1} of spectra. The band at 1 600 cm^{-1} was attributed to aromatic hydrocarbons.

Figures 7 and 8 present the IR spectra obtained for the Base Sub-fractions for all three pitches. For Base Fractions: the major compounds identified were pyridine benzologs, amides and pyrrolic nitrogen compounds.

The infrared spectra of Base Fractions I showed absorption bands at 3 460 cm^{-1} due to N-H absorption of pyrrolic nitrogen compounds, absorption at 1 655 - 1 690 cm^{-1} due probably to amide compounds, and aromatic absorption at 1 600 cm^{-1}.

The infrared spectra of Fractions II show absorption at 1 600 cm^{-1} and 1 655 cm^{-1}. Carbonyl absorption at 1 655 cm^{-1} was assigned to be amide and absorption at 1 600 cm^{-1} indicated the presence of pyridine benzologs and other aromatic compound types. Base Fraction II for Lloydminster pitch displayed an additional band at 1 720 cm^{-1}, which was thought to be an amide carbonyl absorption. The N-H absorption at 3 460 cm^{-1} became a shoulder which indicated an increased hydrogen bonding in the region from 3 450 - 3 100 cm^{-1} due probably to secondary amides.

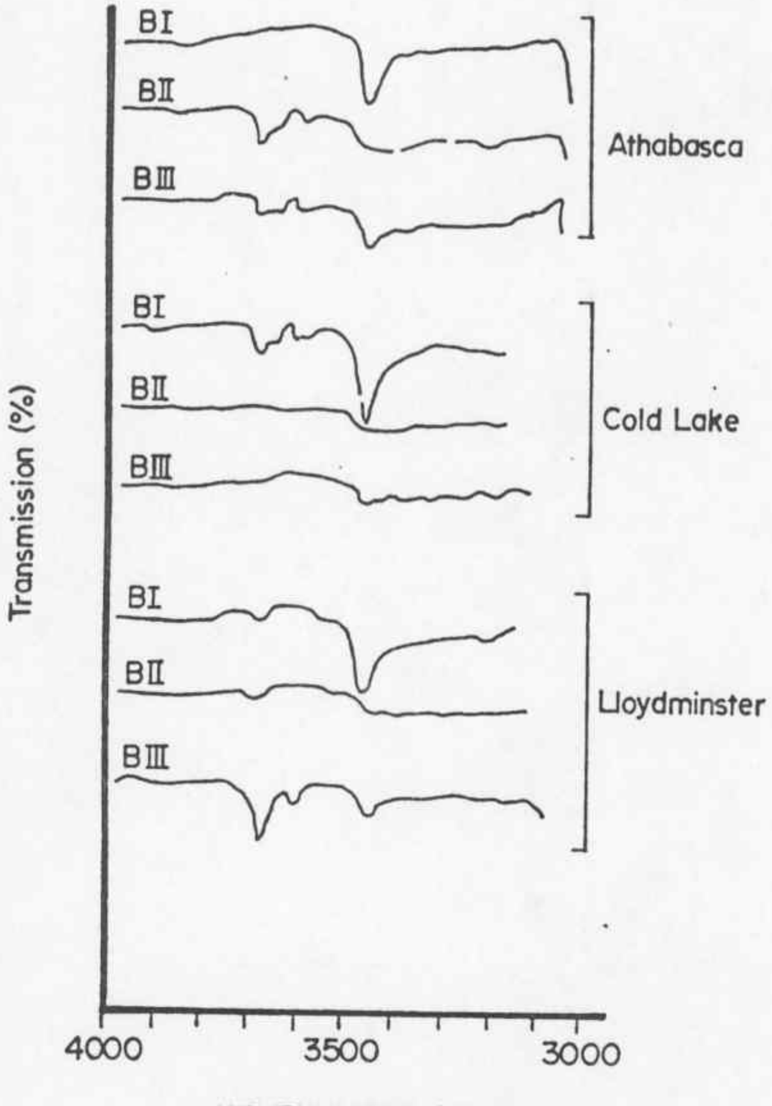
The infrared spectra of Fractions III show the same N-H absorption at 3 460 cm^{-1} with increased hydrogen bonding and absorption bands at 1 595 - 1 600 cm^{-1} characteristic for pyridine benzologs and other aromatic compound types. Strong bases such as pyridine benzologs appeared to be the most predominant basic compound type in Fraction III.

The IR spectra of the Neutral Nitrogen Fractions are presented in Figure 9. The major compound types present in this fraction appear to be amides and pyrrolic nitrogen compounds.

Neutral nitrogen fraction showed a band at 3 460 cm^{-1} due to carbasole and absorption between 1 600 - 1 700 cm^{-1} due to amides. The neutral nitrogen fraction contains pyrrolic compounds and amides that are unreactive to either anion or cation resin but which coordinate with ferric chloride to form a coordination complex. In addition this fraction may contain some aromatic hydrocarbons. The high molecular weights indicated that the molecules are highly associated in solution and/or that the material contains high molecular weight compounds.

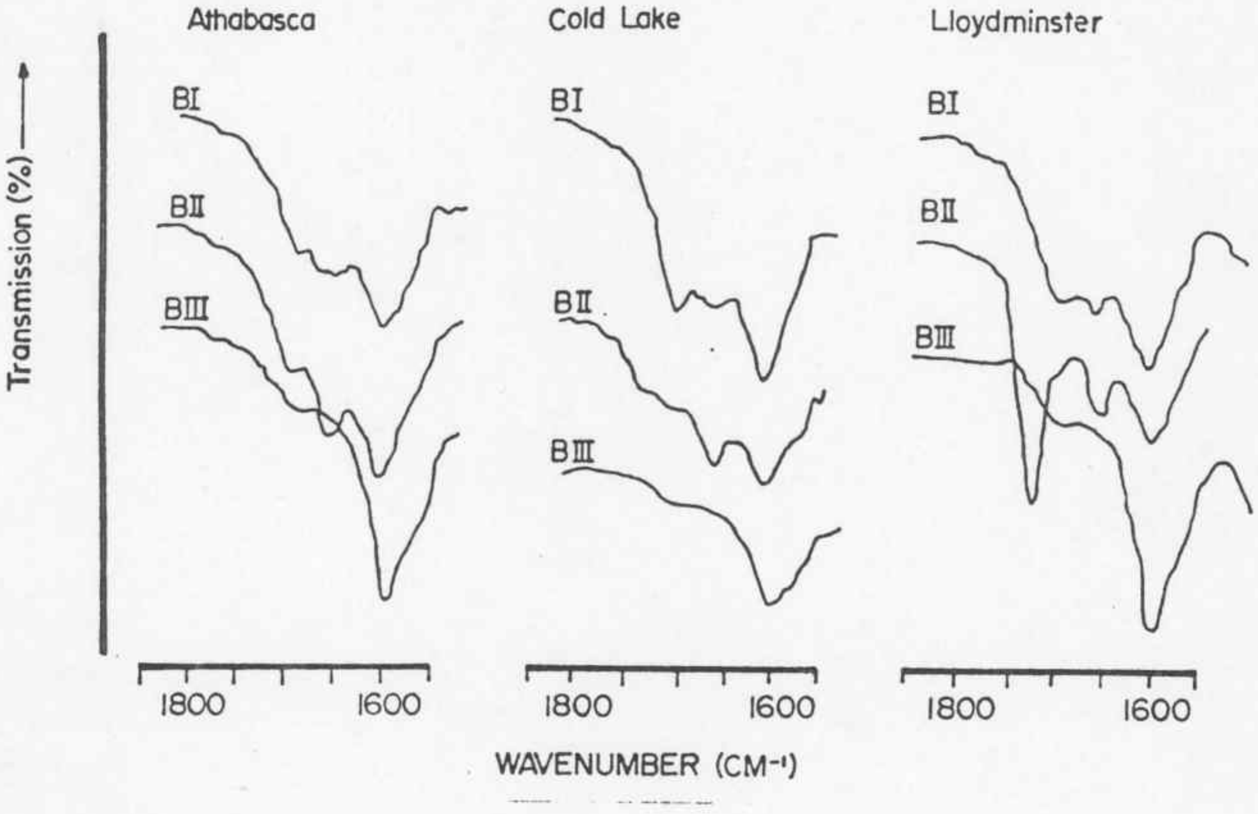
Infrared spectra of base fractions

Figure 7

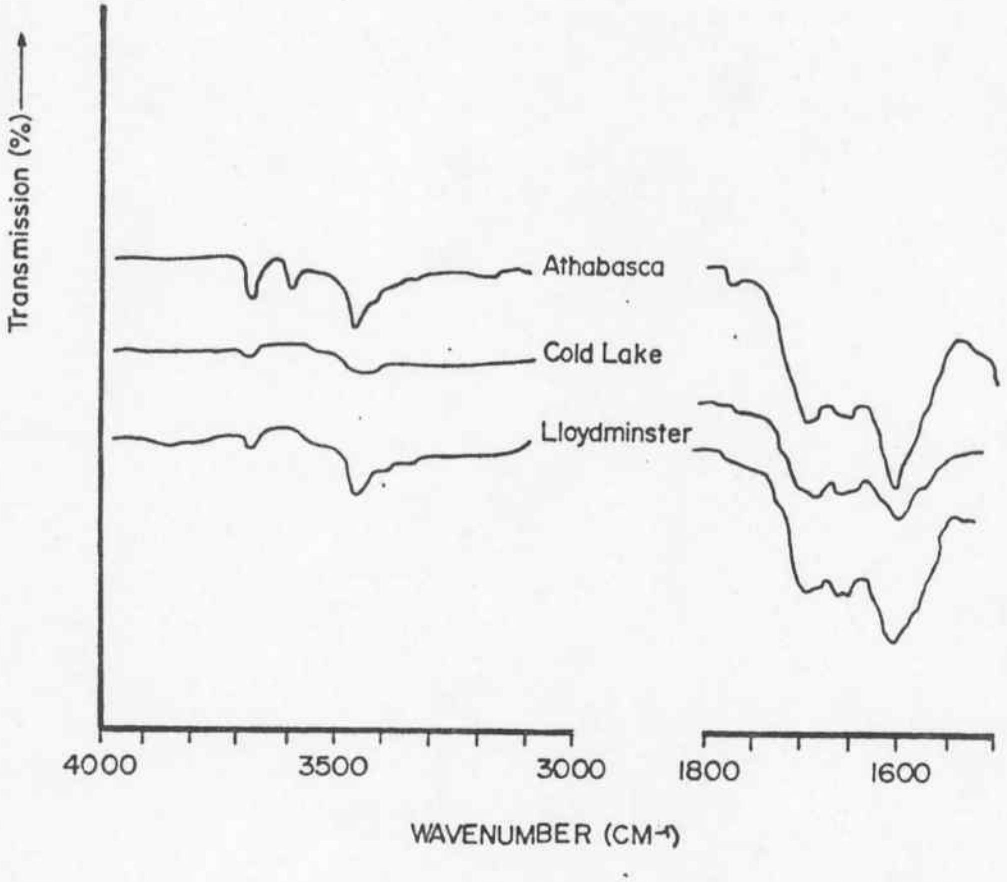


Infrared spectra of base fractions

Figure 8



Infrared spectra of Neutral-Nitrogen fractions Figure 9



In addition to the determination of the molecular weight and elemental composition, the hydrocarbon sub-fractions were subjected to infrared spectrographic methods in order to determine average paraffinic and naphthenic carbon contents (% Cp, % CA, % Cn). The method used was the infrared spectroscopic method for structural group analysis also used by M.A. Poirier and A.E. George for heavy oils and synthetic fuels. The correlation relating absorption coefficient to aromatic and paraffinic content were taken from the study by Baibazarov.

$$\% \text{ Cp} = 62.93\ E_{2850} - 31.54$$

$$\% \text{ CA} = 710.19\ E_{1600} - 11.55$$

$$\% \text{ Cn} = 100 - \% \text{ Cp} - \% \text{ CA}$$

Where Cp, CA and Cn are the paraffinic, aromatic and naphthenic carbon contents respectively; E_{2850} and E_{1600} are the absorption coefficients at 2 850 cm^{-1} and 1 600 cm^{-1}. The absorption coefficients at the respective wavelengths are determined according to the Beer-Lambert law by the following formula:

$$E_{\text{max}} = \frac{\log A/B}{c \times a}$$

Where A and B determine the transmittance value of the absorption band calculated by the baseline method.

c = concentration of the sample (g/L)

a = path length of the cells, (cm)

Carbon tetrachloride (spectral grade) was used as solvent for the 2 850 cm^{-1} region and methylene chloride for the 1 600 cm^{-1} region of the spectrum. The presence of other absorption bands in the neighbourhood of the 2 850 cm^{-1} and 1 600 cm^{-1} bands introduced some ambiguity in the definition of the baseline.

The results presented in Table 9 indicate a predominant naphthenic character in the entire hydrocarbon fraction.

As expected no aromatic carbon was found in the saturate sub-fraction. The paraffinic carbon values between 32.6 (Athabasca) and 43.0% (Cold Lake) with the balance to 100 being naphthenic carbons.

In the monoaromatic sub-fraction the CA % was found to be surprisingly low - only 2 - 5%, while Cn % was about the same as in the saturate sub-fraction.

There seems to be a certain specificity in the Lloydminster heavy oil pitch in the sense that the naphthenic character (Cn %) in both monoaromatic and diaromatic fractions is lower, while the aromatic carbon (CA %) is somewhat higher than in the bitumen derived pitches.

Also the Lloydminster pitch hydrocarbon displays a consistently higher paraffinic character (Cp %) than the bitumen derived pitches.

The carbon type distribution in the polyaromatic-polar sub-fraction which represents the predominant component in all three pitches was found to be similar for the three pitches - namely 71.5 - 75.9% Cn, 18.5 - 22.1% CA and a low 4.2 - 7.8% Cp.

Table 9 Carbon Type Distribution in the Hydrocarbon Fractions

Fraction Type	Pitch Sample	Carbon Type Distribution		
		% Cp	% CA	% Cn
Saturate	Athabasca	32.6	0	67.4
	Cold Lake	43.0	0	57.0
	Lloydminster	40.7	0	59.3
Monoaromatic	Athabasca	29.8	4.4	65.8
	Cold Lake	28.1	2.2	69.6
	Lloydminster	40.9	5.5	53.6
Diaromatic	Athabasca	32.6	11.3	56.0
	Cold Lake	15.9	8.7	75.3
	Lloydminster	33.9	15.9	50.2
Polyaromatic and Polar	Athabasca	6.4	22.1	71.5
	Cold Lake	4.2	19.9	75.9
	Lloydminster	7.8	18.5	73.7

REFERENCES

A.A. Baibazarov, et al
"Spectrophotometric Method for Structural-group analysis of Residual Petroleum Stocks"

Khimiya i Tekhnologiya Topliv i Masel, No. 6, pp 58-60 June 1978

W.E. Haines, C.C. Ward and J.M. Sugihara
"Development of Analytical Techniques for Heavy Hydrocarbons and Related Compounds"

Proceedings of the American Petroleum Institute, Division of Refining, 36th mid-Year Meeting, San Francisco. V. 51, 1971

D.M. Jewell, et al
"Ion-Exchange, Coordination and Adsorption Chromatographic Separation of Heavy-End Petroleum Distillates"

Analytical Chemistry, Vol. 44, No.8, page 1391 July 1972

J.F. McKay, et al
"Petroleum Asphaltenes-Chemistry and Composition"

Symposium of Analytical Chemistry of Tar Sands and Oil Shale presented before the Division of Petroleum Chemistry, Inc. American Chemical Society, New Orleans Meeting, March 20-25, 1977

John F. McKay, et al
"Composition of Petroleum Heavy Ends
Separation of Petroleum >675°C Residues and Characterization of Compound Types in Petroleum >675°C Residues"

Fuel, 1981, Vol. 60, January page 14

M.A. Poirier and A.E. George
"Use of Infrared Spectroscopy for Structural Group Analysis of Heavy Oils and Synthetic Fuels"

CANMET Report 80-72

H. Sawatzky, et al
"Hydrocarbon-type Separation of Heavy Petroleum Fractions"

Fuel, 1976, Vol. 55, January page 16

H. Sawatzky, et al
"Separation of Nitrogenous Materials from Bitumen and Heavy Oils"

CANMET Report 77-10