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Characterization and Utilization of Hydrotreated Products Produced From the
Whiterocks (Utah) Tar Sand Bitumen-Derived Liquid

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Characterization and Utilization of Hydrotreated Products
Produced from the Whiterocks (Utah) Tar Sand
Bitumen-Derived Liquid
by
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ABSTRACT

The bitumen-derived liquid produced in a 4-inch
diameter fluidized-bed reactor from the mined and crushed ore
from the Whiterocks tar sand deposit has been hydrotreated in a
fixed-bed reactor. The purpose was to determine the extent of
upgrading as a function of process operating variables. A
sulfided nickel-molybdenum on alumina hydrodenitrogenation
catalyst was used in all experiments. Moderately severe
operating conditions were employed; that is, high reaction
temperature (617-680 K) high reactor pressure (11.0-17.1 MPa)
and low liquid feed rate (0.18-0.77 HSV); to achieve the desired
reduction in heteroatom content. Detailed chemical structures
of the bitumen-derived liquid feedstock and the hydrotreated
total liquid products were determined by high resolution gas
chromatography - mass spectrometry analyses. The compounds
identified in the native bitumen included isoprenoids; bicyclic,
tricyclic, and tetracyclic terpenoids; steranes; hopanes; and
perhydro-β-carotenes. In addition, normal and branched alkanes
and alkenes and partially dehydrogenated hydroaromatics were
identified in the bitumen-derived liquid. The dominant pyrolysis
reactions were: 1) the dealkylation of long alkyl side chains to
form α - and isoolefins; and 2) the cleavage of alkyl chains
linking aromatic and hydroaromatic clusters. Olefinic bonds
were not observed in the hydrotreated product and monoaromatic
hydrocarbons were the predominant aromatic species. The
properties of the jet fuel fractions from the hydrotreated
products met most of the jet fuel specifications. The cetane
indices indicated these fractions would be suitable for use as
diesel fuels.

Introduction

The alternative fossil energy resources suitable for the production of liquid fuels include coal, oil shale, and tar sands. The bitumen and bitumen-derived liquids produced from tar sands and the shale oil produced from oil shale have been proved superior to hydrogen-deficient coal-derived liquids as potential refinery feedstocks[1]. Commercial scale production of liquid transportation fuels from oil shale has been demonstrated to be feasible by UNOCAL at their Parachute Creek oil shale project[2]. Unfortunately, the project has been terminated due to declining oil prices. In fact, the Suncor and Syncrude Canada, Ltd., plants which produce bitumen from the Athabasca oil sands are the only commercial alternative fossil energy operations in the Western Hemisphere. A long-term solution to the imbalance between United States domestic energy supply and demand could result from the utilization of domestic tar sand, oil shale and coal resources. Thus, development of the technologies required for the production of hydrocarbon liquids from these

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resources should be pursued. The considerable tar sand resource in Utah provides an opportunity for domestic commercial production of asphalt and bitumen-derived liquids.

Naturally occurring bitumen, which can be extracted from oil sands, is a member of the petroleum family that contains compounds ranging from non-polar aliphatic and naphthenic hydrocarbons to highly polar aromatics. Bitumens also contain heteroaromatic species which contain heteroatoms such as nitrogen, sulfur and oxygen. The native Whiterocks (Utah) tar sand bitumen has been separated into several boiling-range fractions for detailed analysis and characterization[3,4]. The lighter fraction, 477-617 K (400-650°F), was evaluated for use as a transportation fuel, and the residue, >617 K (>650°F), has been classified as a viscosity grade AC-10 asphalt. Several physical properties were also measured to evaluate the potential of the 477-617 K fraction as a high density-energy aviation turbine fuel. The detailed chemical structure of two fractions (477-617 K and 617-728 K) from the Whiterocks bitumen was studied by gas chromatography - mass spectrometry (GS-MS). These lower molecular weight fractions were predominantly naphthenic hydrocarbons and contained lesser concentrations of aromatic hydrocarbons. The naphthenic hydrocarbons included alkylcyclohexanes, aklyldecalins, tricyclic terpanes, steranes, tetracyclic terpanes and pentacyclic terpanes. The aromatic constituents were determined to be alkylbenzenes, benzo-monocycloparaffins, and phenyl (cyclohexyl) alkanes. These compounds were similar in nature to those found in the bitumen from Green River oil shale. The proton and carbon-13 NMR characteristics of Whiterocks bitumen were determined by comparing the spectra of the samples to literature assignments. Tentative structure assignments for the pyrolysis products were made based on Curie-point, low-voltage mass spectroscopic (Py-Ms) analysis. The results obtained from proton and carbon-13 NMR, FTIR, Py-MS and GC-MS analyses suggested that the native bitumen consisted mostly of short- (C_1-C_3) and long-(>C_6) alkyl-substituents attached to polycyclic naphthenic, naphtheno-aromatic, and aromatic hydrocarbons. The structure of the high boiling fraction, >811 K, (>1000°F) of the Whiterocks bitumen was characterized by aromatic and heteroaromatic moieties surrounded by long alkyl side chains and naphthenic groups.

Fluidized-bed and rotary-kiln pyrolysis[5] are two potential thermal processes for recovering and upgrading bitumen from oil sands. The fluidized-bed pyrolysis of Utah tar sands has been studied extensively at the University of Utah[6-10]. The tar sand deposits investigated included Sunnyside[6], Whiterocks[7-9], PR Spring[8], Tar Sand Triangle[6], and Circle Cliffs[9,10]. A maximum liquid yield of approximately 70 weight percent was obtained in a bench scale fluidized-bed reactor. The similarity of the major compound types found in shale oil and tar sand bitumens[3,4] suggested that the processes and catalysts developed to upgrade shale oil can also be used to upgrade the bitumens and/or the bitumen-derived liquids produced from tar sands.

A study of the feasibility of hydrotreating the bitumen-derived liquid obtained from thermal decomposition of the Whiterocks tar sand in a fluidized bed reactor has been completed[11,12]. In the present study, we have examined the composition of the bitumen-derived liquid and the hydrotreated products

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using gas chromatography - mass spectrometry (GC-MS). These data coupled with the GC-MS analyses of the native bitumen have been used to identify potential reaction pathways for the processing sequence pyrolysis followed by hydrotreating (pyrolysis-hydrotreating). The hydrotreated products were also fractionated into several boiling range cuts for detailed analysis. The collected data were used to evaluate the upgrading potential of the bitumen-derived liquid and to correlate the hydrotreating process operating variables with the product distribution.

Experimental Methods and Means

Fluidized Bed Pyrolysis Unit

The experimental apparatus, the operating procedures, and the continuous production run in which the bitumen-derived liquid was produced from the mined and crushed ore from the Whiterocks tar sand deposit have been discussed in detail by Sung[9].

Hydrotreater Process Unit

All hydrotreating experiments were performed in a high pressure, high temperature catalyst testing unit during a continuous 1000 hour run. The system was operated in the up-flow mode and the bitumen-derived liquid and hydrogen were introduced at the bottom of the reactor. The up-flow mode permitted nearly isothermal operation of the reactor; that is, the arithmetic and kinetic average temperatures were nearly the same. Further- more, more efficient liquid-solid contacting was attained.

The process operating variables ranges were as follows: reaction temperature, 617-680 K (650-765°F); 0.185 - 0.76 LHSV; total reactor pressure, 11.0-17.2 MPa (1600 - 2500 psig); and H_2/hydrocarbon ratio, 890 $m^3\backslash m^3$ (5000 scf/bbl. A commercially available hydrodenitrogen (HDN) catalyst was used to hydrotreat the bitumen-derived liquid. A description of the experimental apparatus and operating procedures; a description of the catalyst and the catalyst activation procedures; and a summary of the process variable study have been reported by Longstaff, et al[12]. The design, construction and operation of the hydrotreater catalyst testing unit have been discussed in detail by Longstaff[11].

Analysis of Hydrotreated Products

A modified vacuum distillation system was used for the fractionation of the hydrotreated products into three boiling-range fractions (IPB-477 K, 477-617 K, and >617 K). A Vigreux distillation column (40cm long) packed with 5x5 mm glass Rasching rings was placed between a Claisen distillation column and the distillation flask. Elemental analysis and physical properties were determined to complete the characterization of these fractions. Viscosities were determined with a Brookfield cone and plate viscometer (Model LVT) and the refractive index was determined with an Abbe refractometer. Properties such as the heat of combustion, the freeze point, the pour point, the cetane index and the carbon type distribution were determined following the procedures outlined for the standard ASTM tests. Detailed compositional analyses were determined by gas chromatography - mass spectrometry (GC-MS) and Fourier transform infrared (FTIR) spectroscopy.

Simulated Distillation

The boiling point distributions of the hydrotreated products were determined by simulated distillation. The samples were dissolved in dichloromethane and the analyses were performed on a programmed Hewlett-Packard Model 5730 A gas chromatograph: the oven temperature was programmed from 243 to 623 K at 11°C/minute and was held at 623 K for 16 minutes; the injector temperature was initially set at 523 K and raised to 633 K after 12 minutes where it was held for the rest of the run; and the FID detector temperature was 673 K. The column consisted of a U-shaped 45.7 cm x 0.635 cm OD stainless steel tube packed with 3% Dexsil 300 on Anakrom Q. The boiling point temperatures were calibrated with a standard mixture of normal paraffins (C_5 - C_{44}).

Fourier Transform Infrared Spectroscopic Analysis

The FTIR spectra were obtained with a Perkin Elmer 1600 spectrometer which was operated in the transmission mode. Trans-mission spectra of the bitumen-derived liquid and the hydrotreated products were determined in a liquid cell with a path length less than 0.015 mm.

Gas Chromatography-Mass Spectrometry Analysis

The bitumen-derived liquid feed and the hydrotreated total liquid products were analyzed with a gas chromatograph (Hewlett-Packard Model 5890 A) using a fused silica capillary column coated with 5% phenyl methyl silicone bonded stationary phase (30m x 0.25mm ID, DB-5, J & W scientific). The temperature program was ranged from 323 K to 573 K at 3°C min^{-1}, with a hold at 573 K for 20 minutes.

Gas chromatography - mass spectrometry analyses were performed on a Finnigan MAT95 high resolution gas chromatograph/mass spectrometer (Finnigan MAT ICIS II operating system) fitted with a DB-5 gas chromatographic column (30m x 0.25mm ID).

Results and Discussion

The properties of the native Whiterocks bitumen, the bitumen-derived liquid, and the Paraho shale oil[13] are compared in Table 1. The bitumen derived liquid properties were superior to those of the native bitumen, that is, the value of pentane insolubles, viscosity, pour point, Conradson carbon residue, metals content, and average molecular weight were lower than those for the native bitumen. The bitumen-derived liquid had properties similar to those of the Paraho shale oil except that the shale oil had a higher pour point and nitrogen content. The higher pour point can be explained by the higher concentration of normal paraffins[4]. Like shale oil, the bitumen-derived liquid contained few hydrocarbons in the naphtha boiling range.

The bitumen-derived liquid had a high nitrogen content (1.1 wt%); removal of nitrogen was the focus of the bitumen-derived liquid hydrotreating studies. Thus, an HDN catalyst was selected for the bitumen-derived liquid upgrading studies. Since the nitrogen compounds were more refractory than sulfur and oxygen compounds under hydroprocessing conditions, desulfurization and de-oxygenation reactions were of secondary interest.

The effects of reaction temperature at fixed reactor pressure, LHSV and H_2/hydrocarbon ratio; LHSV at fixed reaction temperature

Table 1.   Properties of the Native Whiterocks Bitumen and Bitumen-Derived Liquid and the Paraho Shale Oil.

Properties	Whiterocks Native Bitumen	Whiterocks Bitumen-Derived Liquid	Paraho Shale Oil
Gravity, °API	12.2	18.5	20.2
Viscosity, cps	7,900.(333 K)	450.(298 K)	23.3 (323 K)
Pour Point, K	313	279	305
Conradson Carbon Residue, wt%	8.8	4.7	----
Ash, wt% (ASTM D486)	0.24	----	0.03
Elemental Analysis			
C, wt%	85.8	85.9	84.3
H, wt%	11.6	11.1	11.3
N, wt%	1.1	1.1	2.2
S, wt%	0.4	0.4	0.7
O^a, wt%	1.1	1.5	1.2
Ni, ppm	78	----	----
V, ppm	4	<1	----
As, ppm	2	----	28
H/C Atomic Ratio	1.62	1.55	1.61
Molecular Weight, g mol^{-1}	561	318	328
Pentane Insolubles, wt%	4.0	2.8	0.17^b
Volatility (<811 K), wt%	44.1	82.2	94.0^c

^{a}By difference; ^{b}Heptane insoluble; ^{c}End point 823 K.

reactor pressure and H_2/hydrocarbon ratio; and reactor pressure at fixed reaction temperature, LHSV and H_2/hydrocarbon ratio are presented in Tables 2, 3, and 4, respectively. The material balances ranged from 98 - 102 wt% for all experiments reported in this paper.

Total liquid product nitrogen ranged from 3070 ppm to 43 ppm. The highest nitrogen content was obtained at the base case conditions, i.e., average catalyst bed temperature, 619 K; total pressure, 13.7 MPa; and LHSV 0.5 h^{-1}. The data presented in Tables 2 through 4 indicated that the operating conditions required to produce nitrogen levels in the range from 500 - 1500 ppm, would be as follows: a temperature above 644 K, a reactor pressure above 11.0 MPa and a liquid hourly space velocity of 0.5 h^{-1}.

The effect of reaction temperature on the extent of denitrogenation was determined at a LHSV of 0.5 h^{-1} and a pressure of 13.7 MPa. An increase in reaction temperature resulted in an increase in hydrogen content and API gravity and a decrease in the nitrogen and sulfur contents of the total liquid product (Table 2). The gas, naphtha and middle distillate yields and hydrogen consumption also increased. The data in Table 2 also indicated that cracking of the bitumen-derived liquid occurred during denitrogenation. Thermal cracking was assumed to be minimal at 680 K; however, it could be important if the reaction temperature was above 725 K[14].

The effect of liquid feed rate was determined at a reactor pressure 13.7 MPa and a reaction temperature of 663 K. The results are presented in

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Table 2. Properties of the Hydrotreated Total Liquid Product as a Function of Reaction Temperature

Run Identification Number	16	22	9	7
Operation Conditions:				
Temperature, K	619	644	663	681
Total Pressure, MPa	13.7	13.5	13.7	13.7
LHSV, h^{-1}	0.5	0.5	0.5	0.51
H_2/oil, $m^3 \backslash m^3$	890	890	890	890
H_2 Consumption, $m^3 \backslash m^3$	145	166	181	195
Product Yields, wt%				
$C_1 - C_4$	0.6	1.6	2.8	4.3
C_5 Liquid 98.5	98.3	96.3	94.8	
Total Liquid Product				
Elemental analysis				
C, wt%	86.8	87.0	86.8	86.7
H, wt%	12.1	12.1	12.6	12.8
N, ppm	3070	1631	748	202
S, ppm	271	65	45	16
H/C Atomic ratio	1.68	1.67	1.74	1.77
Gravity, °API	23.2	24.9	26.9	29.8
Pour Point, K	264	249	245	248
Simulated Distillation, (ASTM D2887)				
IBP, K	423	429	306	305
IBP-477 K wt%	3.8	3.4	7.4	9.4
477-617 K, wt%	21.7	19.5	28.7	34.9
617-811 K, wt%	61.5	64.5	55.8	48.1
>811 K, wt%	13.0	12.6	8.1	7.6

Table 3. A decrease in the liquid feed rate resulted in an increase in the API gravity and hydrogen content and in a decrease in the nitrogen and sulfur contents of the total liquid product. The light gas, naphtha and middle distillate yields and the hydrogen consumption also increased. The nitrogen content of the total liquid products produced at LHSV's of 0.5 and 0.77 h^{-1} were 748 and 1434 ppm, respectively.

The liquid product gravities and the product distributions were similar at gas flow rates of 890 and 1250 m^3/m^3. This confirmed the speculation that the effect of the hydrogen-to-hydrocarbon ratio was small above a minimum value when compared to the influence of other variables[15]. A 30.5°API total liquid product was produced at a reaction temperature 680 K, a total pressure of 13.5 MPa, and an LHSV of 0.19 h^{-1}. The hydrogen consumption at these conditions was 277 m^3/m^3 which was similar to that reported for shale oil upgrading[2].

The effect of operating pressure was determined at a reaction temperature of 663 K and an LHSV of 0.5 h^{-1}.

Table 3. Properties of the Hydrotreated Total Liquid Product as a Function of Liquid Hourly Space Velocity

Run Identification Number	26	11	18	17	9	24
Operation Conditions						
Temperature, K	680	663	664	663	663	663
Total Pressure, MPa	13.5	13.7	13.6	13.7	13.7	13.8
LHSV, h^{-1}	0.19	0.20	0.37	0.35	0.50	0.77
H_2/oil, m^3/m_3	990	890	890	1250	890	890
H_2 Consumption, m^3/m^3	277	277	239	198	181	147
Product Yields, wt%						
C_1-C_4	7.5	5.4	3.2	5.4	2.8	3.3
C_5 Liquid	93.1	94.5	96.3	93.8	96.3	95.6
Total Liquid Product,						
Elemental analysis						
C, wt%	86.0	86.5	86.9	86.7	86.8	86.9
H, wt%	13.2	13.0	12.6	12.6	12.6	12.3
N, ppm	43	186	686	-	748	1434
S, ppm	16	18	77	181	45	349
H/C Atomic ratio	1.84	1.80	1.74	1.75	1.74	1.70
Gravity, °API	35.0	30.2	27.8	28.0	26.9	25.7
Pour Point, K	258	261	244	-	245	243
Simulated Distillation,						
(ASTM D2887)						
IBP, K	371	380	400	403	396	417
IBP-477 K, wt%	13.9	9.2	6.5	6.4	7.4	4.1
477-617 K, wt%	44.5	36.7	28.9	28.9	28.7	24.8
617-811 K, wt%	38.7	48.7	56.3	56.8	55.8	59.5
> 811 K, wt%	2.9	5.4	8.3	7.9	8.1	11.6

The results are summarized in Table 4. The product distribution changes between 11.0 - 16.9 MPa were marginal. This suggested there would be no advantage to increasing the reactor pressure from 13.7 to 16.9 MPa; since the extent of denitrogenation was almost the same, despite the increase in hydrogen consumption (~ 90 m^3/m^3).

These results indicated that the conditions for effective denitrogenation of the bitumen-derived liquid were similar to that for shale oil using conventional and/or unconventional HDN catalysts[13,16,17]. These conditions were as follows: reaction temperature, 658 to 700 K; total pressure, 12.4 to 15.2 MPa; and LHSV, 0.5 - 0.6 h^{-1}.

The yields and product inspections for the various boiling range fractions distilled from the total liquid product produced when the bitumen-derived liquid was hydrotreated over an HDN catalyst are summarized in Table 5. The properties of the naphtha fractions from the hydrotreated bitumen-derived liquid were similar to those of the naphtha fractions from hydrotreated shale oil[2,13].

Table 4.Properties of Hydrotreated Total Liquid Product as a Function of Operating Pressure

Run Identification Number	15	9	28	20	13
Operating Conditions:					
Temperature, K	665	663	662	662	664
Total Pressure, MPa	11.0	13.7	13.8	15.5	17.1
LHSV, h^{-1}	0.50	0.50	0.51	0.50	0.48
H_2/oil, m^3/m^3	890	890	890	890	890
H_2 Consumption, m^3/m^3	134	181	155	244	287
Product Yields, wt%					
$C_1 - C_4$	4.6	2.8	3.4	4.1	4.1
C_5 Liquid	94.1	96.3	95.5	95.6	95.7
Total Liquid Product					
Elemental Analysis					
C, wt%	86.9	86.8	86.9	86.7	87.0
H, wt%	12.0	12.6	12.5	12.6	12.6
N, ppm	1260	748	1085	942	727
S, ppm	28	45-	213[a]	37	
H/C Atomic ratio	1.71	1.74	1.73	1.74	1.74
Gravity, °API	26.6	26.9	26.8	27.1	27.7
Pour Point, K	264	245	260	259	250
Simulated Distillation, (ASTM D2887)					
IBP, K	412	396	406	412	403
IBP-477 K, wt%	5.2	7.4	5.0	5.2	6.1
477-617 K, wt%	27.8	28.7	25.1	27.5	27.9
617-811 K, wt%	58.2	55.8	59.9	57.6	56.3
>811 K, wt%	8.8	8.1	10.0	9.7	9.7

[a] Sulfur high due to dissolved H_2S.

The API gravities of the naphtha fractions distilled from the hydrotreated bitumen-derived liquid were lower than those of light Arabian naphthas[13]. This suggested that the naphthene and aromatic contents of the naphtha fractions distilled from the hydrotreated total liquid product were significantly higher than that of Arabian light crude naphthas. This was confirmed by GC-MS analysis of the bitumen-derived liquid and the hydrotreated total liquid product. The naphtha fraction from the hydrotreated bitumen-derived liquid appeared to be a superior reformer feedstock than petroleum derived naphthas for the production of petrochemicals and gasoline.

It has been shown that shale oil would be an excellent source of JP-4, JP-5, JP-8 and Jet A fuels and diesel fuel[2,13]. The middle distillate fractions of the hydrotreated bitumen-derived liquid exhibited acceptable properties for possible use as jet and diesel fuels. The properties of the middle distillate fractions met most Jet A specifica-tions except for the freezing point of the fraction produced in run 20 which was 2°C high (Table 5). Since these middle distillates had higher end points than were specified for the various

Table 5. Yields and Inspections of Boiling Range Fractions Distilled from the Hydrotreated Bitumen-Derived Liquid

Run Identification No.	11	18	20
Nitrogen, ppm	186	686	943
Sulfur, ppm	18	77	213
Catalyst Bed Temperature, K	663	664	663
LHSV, h^{-1}	0.20	0.37	0.50
Total Pressure, MPa	13.7	13.6	15.5
Product Distribution & Yields, wt%			
C_1	1.1	0.8	1.0
C_2	1.1	0.8	1.1
C_3	1.7	1.1	1.5
$i-C_4$	0.5	0.5	0.5
$n-C_4$	0.9	0.1	0.1
C_5-477 K	7.2	6.9	6.8
477-617 K	38.9	29.9	26.4
>617 K	49.6	59.5	62.5
C_5-477 K product			
Gravity, °API	53.8	49.9	51.2
Carbon, wt%	85.4	85.8	85.6
Hydrogen, wt%	14.3	14.1	14.1
H/C atomic ratio	2.00	1.97	1.98
477-617 K product			
Gravity, °API	35.6	34.7	35.0
Carbon, wt%	86.5	86.2	86.6
Hydrogen, wt%	13.5	13.2	13 3
H/C atomic ratio	1.87	1.84	1.84
Aniline point K, (est.)	331	327	331
Molecular weight, g mol^{-1} (est.)	192	189	194
Freezing point, K	232	230	235
Viscosity, 311 K, cps	1.97	1.94	1.89
Viscosity, 311 K, cSt (est)	2.36	2.32	2.26
Cetane index, (ASTM D976-80)	45.5	43.8	44.5
Net of heat of combustion			
BTU/lb_m	18,390	18,450	18,470
BTU/gal	130,000	131,100	131,000
Carbon Distribution, wt% (ASTM D3238)			
C_p	42.5	44.9	46.1
C_N	38.5	35.8	35.1
C_A	19.0	19.3	18.8
Molecular Type Distribution, mole % (API 2B 4.1)			
X_p	0.265	0.269	0.286
X_n	0.527	0.498	0.474
X_a	0.208	0.233	0.240

Table 5. Yields and Inspections of Boiling Range Fractions Distilled from the Hydrotreated Bitumen-Derived Liquid (continued)

TBP Distillation, K (ASTM D86)			
IBP/5	429/455	443/471	444/465
10/30	469/502	475/490	476/503
50	527	527	528
70/90	549/575	546/570	549/578
95/end point	586/591	583/586	590/595
617 K - End point products			
Gravity, °API	23.6	21.7	21.2
Carbon, wt%	87.2	87.2	87.5
Hydrogen, wt%	13.0	12.7	12.7
H/C atomic ratio	1.79	1.74	1.74
Viscosity, 311 K, cps	98.1	153.4	209.2
Viscosity, 311 K, cSt (est.)	108.7	166.8	228.0
Aniline point, K (est.)	360	358	357
Molecular weight, g mol^{-1} (est.)	380	385	382
K Factor (est.)	11.8	11.8	11.7
Pour Point, K	293	290	290
Molecular type distribution mole% (API 2B 4.1)			
X_p	0.436	0.433	0.422
X_n	0.399	0.374	0.394
X_a	0.165	0.193	0.185
Simulated distillation, (ASTM D2887)			
IBP, K	581	583	579
10 wt%, K	628	623	624
30 wt%, K	674	674	675
50 wt%, K	716	723	723
70 wt%, K	757	764	761
80 wt%, K	783	791	786
>811 K, wt%	11.2	13.8	11.6

jet fuels the freeze point could be adjusted by reducing the end point. The high heating value per unit volume indicated the potential of these fractions as a source of high density-energy jet fuels after mild hydrofinishing. In addition, the cetane numbers of these middle distillate fractions indicated that they could be used as diesel fuels.

The 617 K plus hydrotreated bitumen-derived liquid contained predominately normal and branched paraffins, polycyclic naphthenes and monoaromatics with polycyclic structure. The abundance of steranes, tricyclic, tetracyclic, and

pentacyclic terpenoids, and normal (C_{17}-C_{32}) and isoprenoid (C_{17}-C_{28}) alkanes in the 617 K plus fraction of the hydrotreated bitumen-derived liquid indicated that this fraction would be an acceptable fuels hydrocracker feedstock. In addition, this fraction would be an acceptable catalytic cracker feedstock. The compounds identified in the 617 K plus fraction would be expected to crack at a high rate in an FCC unit with low coke make. A hydrocracker-FCC combination would provide flexibility and produce high quality transportation fuels from this gas oil fraction[18].

A number of specialty products such as lubricating and white oils could also be produced from this 617 K plus fraction by additional hydrotreating and hydrogenation[19-22].

FTIR Analysis

The results from FTIR analyses indicated that the bitumen-derived liquid feed and the hydrotreated total liquid product were similar to the native bitumen with only minor differences[3]. The band at 3475 cm^{-1} was assigned to pyrollic N-H. Alkylindoles which have been identified by GC-MS analysis were presumed to be the type of compound which contributed to this band. The 3475 cm^{-1} band disappeared at severe hydrotreating conditions, that is, at low liquid feed rate (0.2 LHSV) and a reaction temperature above 664 K. This suggested that the liquid flow rate and reaction temperature exert a more significant influence on the removal of pyrollic types of nitrogen compound than total pressure.

The band near 1700 cm^{-1} which has been attributed to C=O stretching in carboxylic acids was not observed in the bitumen-derived liquid; however, there was a band at 1712 cm^{-1}. This band was attributed to C=O stretching in dialkyl or cyclic ketones or aryl aldehydes[23]. This band was not detected in the hydrotreated total liquid product. This inferred that nitrogen compounds have lower reactivity than oxygen compounds at hydroprocessing conditions. Evidence for the presence of α-olefins in the bitumen-derived liquid feed was found in the absorbance bands at 988.4 and 908.8 cm^{-1}, which were attributed to the CH and CH_2 out-of-plane deformation ($CRH=CH_2$). The band at 885.6 cm^{-1} was due to CH out-of-plane deformation in $CR_1R_2=CH_2$[23]. These three bands were not observed in the spectra for the hydrotreated total liquid products.

Gas Chromatography-Mass Spectrometry

Identification of individual compounds was based on the comparison to known spectra from the literature or were tentatively assigned based on interpretation of the mass spectrum[24-42]. The task of identifying each individual compound was difficult due to the co-elution of several compounds at the same retention time. However, fragmentation patterns were compared to those of known compounds, and in particular to the types of compounds known to be present in similar materials. The structures for individual compounds identified in the bitumen-derived liquid and the hydrotreated total liquid products are summarized in the Appendix. The hydrotreated bitumen-derived liquid consisted primarily of saturated compounds, such as alkanes and cycloalkanes. It also contained low concentrations of aromatic compounds.

Alkanes and Alkenes

High concentrations of alkanes were detected in the hydrotreated bitumen-derived liquid. These compounds were presumed to be derived from the cleavage of side chains on naphthenic, naphtheno-aromatic, and

aromatic species because only small concentrations of alkanes were identified in the native Whiterocks bitumen. Normal alkanes ranging from C_7 to C_{32X}. were identified in the hydrotreated products. In addition, isoprenoid alkanes ranging from C_9 to C_{28} were also identified in the hydrotreated products as evidenced by the intense ion peaks at m/e 113, 141 and 183. α-Olefins which had similar structures were identified in the bitumen-derived liquid. Examples of these compound-types are represented in the Appendix: structures (I) through (X).

Monocyclic Compounds

The native Whiterocks bitumen, contained traces of hydrocarbons boiling under C_{10}[3]. On the contrary, about 3 to 14 wt% of in the bitumen-derived liquid and the hydrotreated total liquid products boiled in the naphtha range. The hydrotreated products contained predominately polymethylated cyclohexanes and benzenes. This naphtha would be an excellent reformer feedstock. Examples of these types of compounds are represented by structures (XI) to (XV) in the Appendix. Structures (XI) and (XV) were probably derived from carotenoid (tetraterpenoid) compounds. Dimethylstyrene (dimethylvinylbenzene) was identified in the bitumen-derived liquid.

Bicyclic Compounds

A significant number of bicyclic compounds, i.e., structures (XVII) to (XXVI) in the Appendix, were identified in the bitumen-derived liquid and in the hydrotreated total liquid products. Unsubstituted and substituted decalins, hydrindans, indans, and tetralins were identified in the hydrotreated total liquid product. In addition, unsubstituted and substituted indenes, dihydronaphthalenes, and naphthalenes were identified in the bitumen-derived liquid. Some of these compounds were not identified in the native bitumen. This observation suggested that most of these bicyclic compounds were derived from tricyclic diterpanes, steranes and hopanes through opening of ring C or ring B during thermal cracking or maturation. Several phenyl(cyclohexyl) alkanes, structures (XXVIII) and (XXIX), were also identified in the hydrotreated total liquid products. These unique compounds were also identified in the native Whiterocks bitumen[3] and in the Green River shale oil[29].

Tricyclic Compounds

Several phenanthrene derived compounds were identified in the bitumen- derived liquid and in the hydrotreated total liquid products. These included alkylated perhydrophenanthrenes, dihydrophenanthrenes and phenanthrenes. It has been suggested the tricyclic terpenoid alkanes (XXVI) were derived from biodegradation of hexaprenol or cheilanthatriol[34,41]. In addition, indan (cyclohexyl) alkanes (XXXVI) were found in both the bitumen-derived liquid and in the hydrotreated total liquid products. It is believed that these compounds were derived from steranes via degradation. These type of compounds have also been identified in the Green River shale oil[29].

Tetracyclic Compounds

Two types of tetracyclic compounds were identified in the bitumen-derived liquid and in the hydrotreated total liquid products. Steranes were the most abundant component of this type. Cholestanes, ergostanes, stigmastanes and a C_{23}

12

sterane were among the species identified. Aromatized steranes (XXXV) were also identified in the hydrotreated products. Several 17,21-secohopanes, structures (XXXIII) and (XXXIV), were also identified in the bitumen-derived liquid and in the hydrotreated total liquid product. These compounds were also identified in the native Whiterocks bitumen[3], P.R. Spring bitumen[30] and crude oil[33]. The presence of 17,21-secohopanes which have been identified in recent or immature sediments may be explained by two possible routes: (1) a thermo-catalytic degradation of pentacyclic hopane precursors during geological maturation, or (2) a microbial opening of ring E of hopanoids, that is, oxidation of hop-17(21)-enes, at an early stage of diagenesis, followed by a geochemical reduction to the corresponding alkanes[33].

Pentacyclic Compounds

The triterpenoid alkanes, gammaceranes and hopanes (C_{27}, C_{29}-C_{35}), were identified in the bitumen-derived liquid and the hydrotreated total liquid product. These compounds were also detected in the native bitumen. This suggested that these compounds were probably quite stable under thermal conditions. No aromatized hopanes were identified in the bitumen-derived liquid. The absence of C_{28} hopanes has been explained by an energetically unfavored two-fold C-C bond cleavage at the same carbon atom in the side chain[39].

Tetraterpenoids

The compound represented by structure (XXXIX), was identified in the bitumen-derived liquid. This compound was probably derived from perhydro-β-carotene and has also been identified in Green River shale oil[28].

Hetroatom Species

Several oxygenated compounds were identified in the native Whiterocks bitumen. These species included benzolfuran ($C_8 H_6 O$); dimethylhydroxy-tetralins ($C_{12} H_{16} O$); benzodicycloparaffinic carboxylic acids ($C_{16} H_{20} O_2$; $C_{17} H_{22} O_2$; $C_{20} H_{28} O_2$); and pentacyclic carboxylic acid ($C_{28} H_{26} O_2$). Alkyl indole and quinoline were also detected in the native bitumen and in the bitumen-derived liquid.

Pyrolysis-Hydrotreating Reaction Pathways

The task of identifying the thermal reaction pathways for bitumen was difficult due to the complexity of the native bitumen. Furthermore, the task was hampered by the lack of structure information for the heavy ends (>811 K). Despite the difficulties, several reaction pathways were identified by combining the data gathered from previous studies[3,4] and present study. The reactions included dealkylation, dehydrogenation, polymerization and condensation, and decarboxylation.

The normal and branched (mostly isoprenoid) alkanes and normal and branched-1-alkenes generated in the pyrolysis reactions originated as alkyl groups attached to aromatic rings and/or from alkyl bridges between two aromatic clusters, two naphthenic clusters, and/or one aromatic cluster and one naphthenic cluster in the high boiling fraction of the bitumen. The ^{13}C NMR spectrum of the native Whiterocks bitumen clearly indicated the presence of long alkyl chains and/or alkyl bridges[4]. Since alkenes were not identified in the 811 K minus fraction of the native bitumen, they

must have formed via pyrolysis reactions.

Dealkylation of alkyl aromatics is thought to occur via cleavage of the benzylic C-C bond in the alkyl side chains:
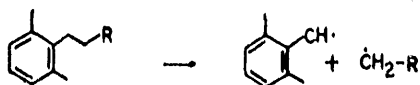
This is followed by an intermolecular hydrogen transfer reaction to give shorter chain alkyl aromatics and aliphatic fragments.
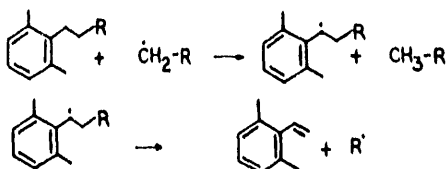
The presence of alkyl indenes, d i h y d r o n a p h t h a l e n e s , dihydrophenanthrenes, alkyl naphthalenes and phenanthrenes, s u g g e s t e d t h a t s t e p - w i s e dehydrogenation of hydroaromatics occurred:
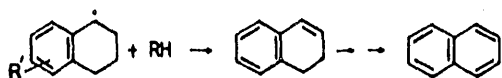
Hydrogen was produced during the pyrolysis of tar sand. The formation of hydrogen was believed to have occurred via a gas phase reaction, coincident with light oils production and a solid reaction, associated with the formation of the carbonaceous residue on the sand grains[43]. The clays in the solid substrate have been activated at pyrolysis conditions and may catalyze polymerization and condensation of aromatics and dehydrogenation of napthenes and hydroaromatics during pyrolysis. The formation of cyclic ketones was confirmed by FTIR analysis. This suggested that air may have been introduced into the pyrolysis reactor. The oxidation

reaction could have taken place on the mineral matter comprising the substrate or on the carbonaceous residue.

Small amounts of carbon dioxide were detected in the produced gases during pyrolysis of the Whiterocks tar sand. It was presumed the CO_2 was produced by thermal decomposition of carboxylic acid functional groups present in the native bitumen. The decomposition of R-COOH bonds readily occurs at the pyrolysis operating temperatures (723 - 823 K)[43]. It was presumed that the CO_2 concentration would have been higher if the source had been mineral carbonates which were present in the reservoir rock. Hydrogenation, hydro-genolysis and heteroatom removal were the principal reactions which occurred in the hydrotreater. The absence of olefins in the hydrotreated products and the heat released in the inlet region of the catalyst bed, suggested that hydrogenation of olefinic bonds has occurred readily during hydroprocessing. The predominance of hydro-aromatic species in the total liquid product indicated that polycyclic aromatics underwent partial hydrogenation. It has been proposed that the naphtha and middle distillate fractions were formed via thermal, rather than catalytic, reaction[14,44]; however, at temperatures below 680 K the catalytic reactions should dominate.

Conclusions

The following conclusions were drawn from the work reported in this paper:

1. The major compound types in the hydrotreated bitumen-derived liquids were n-alkanes (C_7-C_{32}),

branched alkanes (C_7 - C_{28}), polyalkylated cyclohexanes, benzenes, hydrindans, indans, decalins, tetralins, perhydrophenanthrenes and perhydrochrysenes, steranes, and hopanes.

2. The naphtha fraction of the hydrotreated bitumen derived liquid would be an excellent feedstock for catalytic reforming due to the abundance of polymethylated cyclohexanes and benzenes.

3. The gas oil fraction (617 K plus) of the hydrotreated total liquid product would be an excellent feedstock for a fluid catalytic cracker and/or a hydrocracker. Low coke and gas makes and high conversion to napthas and middle distillates would be expected for catalytic cracking because of the abundance of saturated compounds (normal and isoprenoid alkanes and cyclic terpenoid alkanes) and the low concentration of monoaromatics in this fraction.
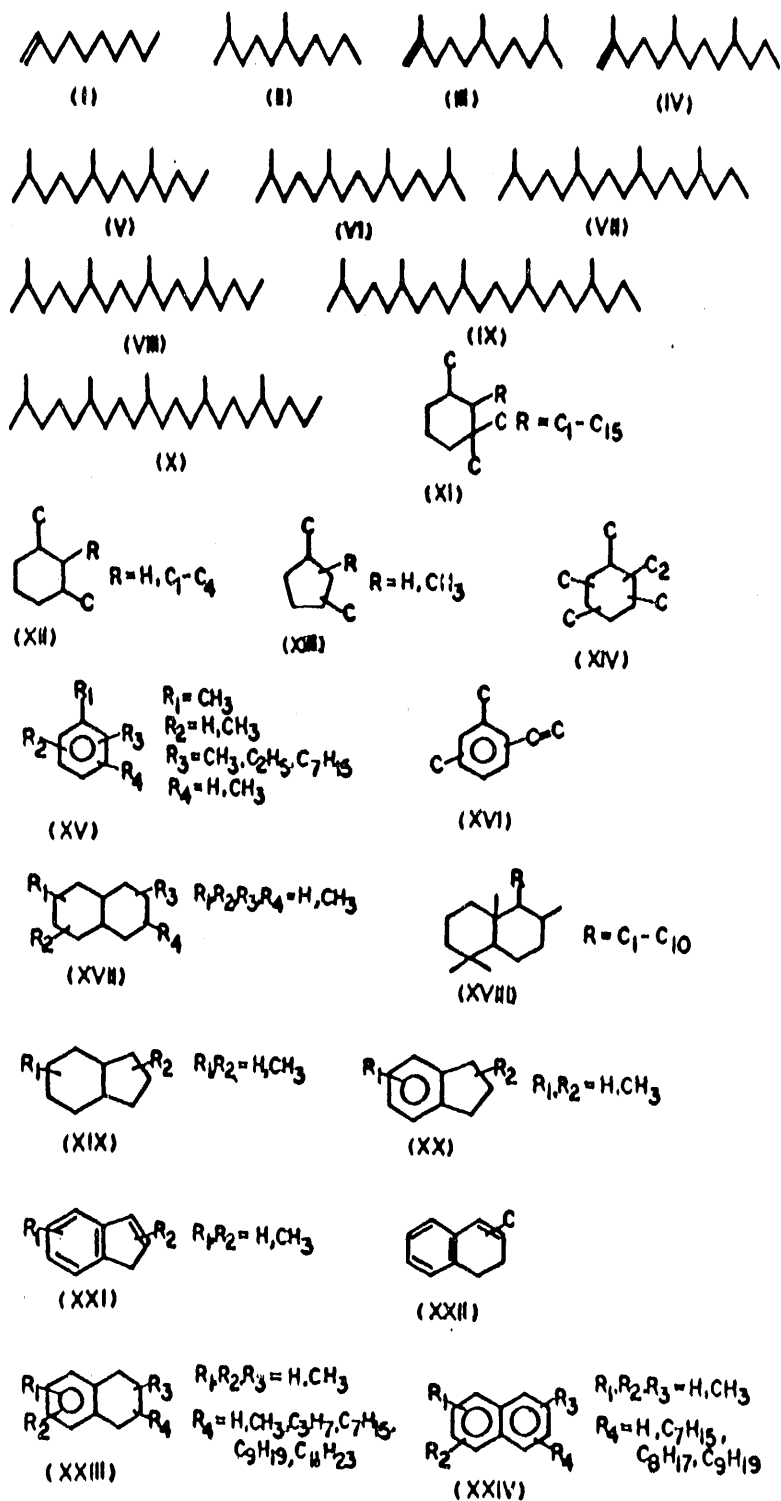
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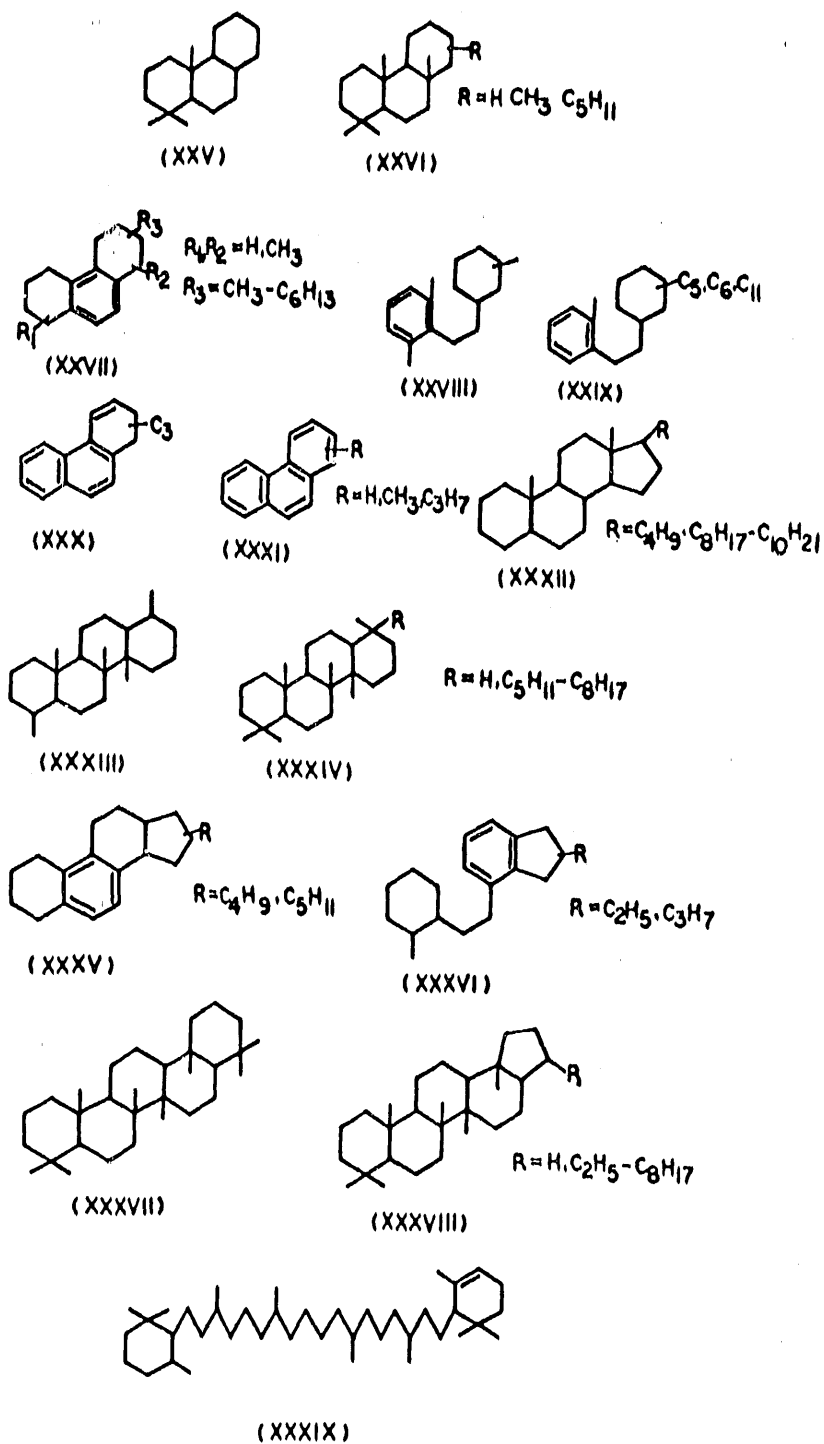
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Appendix: Tentative Structure Assignments of Species Present in the Bitumen-Derived Liquid and the Hydrotreated Total Liquid Product

(I)   (II)   (III)   (IV)

(V)   (VI)   (VII)

(VIII)   (IX)

(X)

$R = C_1 - C_{15}$

(XI)

$R = H, C_1 - C_4$

(XII)

$R = H, CH_3$

(XIII)

(XIV)

$R_1 = CH_3$
$R_2 = H, CH_3$
$R_3 = CH_3, C_2H_5, C_7H_{15}$
$R_4 = H, CH_3$

(XV)

(XVI)

$R_1, R_2, R_3, R_4 = H, CH_3$

(XVII)

$R = C_1 - C_{10}$

(XVIII)

$R_1, R_2 = H, CH_3$

(XIX)

$R_1, R_2 = H, CH_3$

(XX)

$R_1, R_2 = H, CH_3$

(XXI)

(XXII)

$R_1, R_2, R_3 = H, CH_3$
$R_4 = H, CH_3, C_3H_7, C_7H_{15},$
$C_9H_{19}, C_{11}H_{23}$

(XXIII)

$R_1, R_2, R_3 = H, CH_3$
$R_4 = H, C_7H_{15},$
C_8H_{17}, C_9H_{19}

(XXIV)

(XXV)

(XXVI) $R = H \ CH_3 \ C_5H_{11}$

(XXVII) $R_1R_2 = H, CH_3$
$R_3 = CH_3 - C_6H_{13}$

(XXVIII)

(XXIX) C_5, C_6, C_{11}

(XXX) C_3

(XXXI) $R = H, CH_3, C_3H_7$

(XXXII) $R = C_4H_9, C_8H_{17} - C_{10}H_{21}$

(XXXIII)

(XXXIV) $R = H, C_5H_{11} - C_8H_{17}$

(XXXV) $R = C_4H_9, C_5H_{11}$

(XXXVI) $R = C_2H_5, C_3H_7$

(XXXVII)

(XXXVIII) $R = H, C_2H_5 - C_8H_{17}$

(XXXIX)

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