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Hydrotreating the Bitumen-Derived Hydrocarbon Liquid Produced in a
Fluidized-Bed Pyrolysis Reactor

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HYDROTREATING THE BITUMEN-DERIVED HYDROCARBON LIQUID
PRODUCED IN A FLUIDIZED-BED PYROLYSIS REACTOR

by

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ABSTRACT

The pyrolysis of bitumen-impregnated sandstone produces three primary product streams: C_1-C_4 hydrocarbon gases, a C_5^+ total liquid product, and a carbonaceous residue on the spent sand. The bitumen-derived hydrocarbon liquid was significantly upgraded relative to the native bitumen: it had a higher API gravity, lower Conradson carbon residue, asphaltene content, pour point and viscosity and a reduced distillation endpoint relative to the native bitumen. The elemental composition was little different from that of the native bitumen except for the hydrogen content which was lower. Thus, integration of the bitumen-derived liquid into a refinery feedstock slate would require that it be hydrotreated to reduce the nitrogen and sulfur heteroatom concentrations and to raise the atomic hydrogen-to-carbon ratio.

The bitumen-derived liquid produced in a 4-inch diameter fluidized-bed reactor from the Whiterocks tar sand deposit has been hydrotreated in a fixed-bed reactor to determine the extent of upgrading as a function of process operating variables. The process variables investigated included total reactor pressure (11.0-17.2 MPa (1600-2500 psig)); reactor temperature (617-680 K (650-765°F)) and liquid hourly space velocity (0.18-0.77 LHSV). The hydrogen/oil ratio was fixed in all experiments at 890 m^3/m^3 (5000 SCF H_2/bbl). A sulfided Ni-Mo on alumina hydrodenitrogenation catalyst was used in these studies.

The extent of denitrogenation and desulfurization of the bitumen-derived liquid was used to monitor catalyst activity as a function of process operating variables and to estimate the extent of catalyst deactivation as a function of time on-stream. The apparent kinetics for the nitrogen and sulfur removal reactions were determined. Product distribution and yield data were also obtained.

INTRODUCTION

The recovery of hydrocarbon values from Utah's oil sands will occur by a combination of in-situ thermal EOR and mining-surface recovery techniques. The potential mining-surface recovery processes include aqueous separation,[1,2] pyrolysis,[3,4], and solvent extraction[5-7]. The separation and extraction processes produce the native bitumen whereas the pyrolysis processes produce a bitumen-derived hydrocarbon liquid. The integration of the produced bitumens and/or bitumen-derived hydrocarbon liquids into the economy would likely be accomplished by using the native bitumens as asphalt base stocks[8,9] and/or as refinery feedstocks and by using the bitumen-derived liquids as refinery feedstocks. The high nitrogen content of the Uinta basin bitumens and the bitumen-derived liquids, 0.8-1.2 wt%, indicated that

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hydrotreating would be required as a primary upgrading process. The bitumen-derived hydrocarbon liquid produced during the fluidized bed pyrolysis of the mined ore from the Whiterocks tar sand deposit[9] was used as the hydrotreater feedstock in this study.

The Whiterocks tar sand deposit is located in Sections 17-20 Township 2 North, Range 1 East in the Uinta Basin of northeastern Utah. The Whiterocks tar sand was obtained from the Fausett mine/pit on the Western flank of the deposit in Sections 18 and 19. The ore was mined from the surface of the pit after removal of the first 15 or 25 feet of the ore body. Drum quantities were obtained by hand loading higher grade, unweathered material. The ore was crushed and screened prior to being used as feed sand in the fluidized bed pyrolysis production run. The physical and chemical properties of the native bitumen and the produced bitumen-derived hydrocarbon liquid are presented in Table 1[10].

Table 1
Analysis of the Native Bitumen and the
Bitumen-Derived Liquid from the Whiterocks
Tar Sand Deposit

Source	Native Bitumen	Bitumen-Derived Liquid Product
Bitumen content wt%	8.5	--
Product Yields, wt%		
C1 - C4 Gas	--	29.3
C5+ Liquid	--	44.7
Carbonaceous Residue	--	25.0
Gravity, API	11.9	18.5
Density (60°F), g/cm³	0.985	0.943
Heat of Combustion, BTU/lb	19692.	18750.
Viscosity, cps	2665. @ 358 K	45.4 @ 289 K
Pour point, K (°F)	338. (149)	253. (-5)
Conradson carbon residue wt%	8.1	4.6
Simulated Distillation		
Volatility, wt%	40.5	82.2
IBP, K	489	414
IBP-417 K, wt%	0.0	4.7
417-617 K, wt%	4.9	18.3
617-811 K, wt%	35.6	59.0
> 811 K, wt%	59.9	17.5
Elemental Analysis		
C, wt%	85.1	86.0
H, wt%	12.3	11.1
O, wt%	1.1	1.5
N, wt%	1.2	1.12
S, wt%	0.3	0.32
Atomic H/C Ratio	1.73	1.55

The objective of this investigation was to conduct a process variable study related to the hydrotreating of the bitumen-derived liquid product. The process variables studied included the reactor temperature, the total reactor pressure, the liquid hourly space velocity and the hydrogen partial pressure.

EXPERIMENTAL METHODS AND MEANS

Fluidized Bed Pyrolysis System

The bitumen-derived liquid used in the hydrotreating studies was produced from the Whiterocks tar sand ore in a large diameter fluidized bed pyrolysis reactor which was operated continuously over a 25 day period. The reactor temperature ranged from 773 to 813 K, and the average feed sand retention time was 17.2 minutes during the course of the production run. The bitumen-derived liquid was significantly upgraded relative to the native bitumen (Table 1): 18.5 °API versus 11.9°API; a viscosity of 85.4 cps @ 289 K, versus 2665 cps @ 358 K; a volatility (<811 K [<1000°F]) of 82.2 wt.% versus 40.5 wt.%; a Conradson carbon residue of 4.6 wt% versus 8.1 wt%; etc., respectively. The atomic hydrogen-to-carbon (H/C) ratio of the bitumen-derived liquid was lower than that of the native bitumen. This reduction was related to dealkylation and hydroaromatic dehydrogenation reactions during pyrolysis which resulted in the production of a more aromatic hydrocarbon liquid and consequently a lower H/C ratio. Furthermore, the asphaltene fraction in the native bitumen was assumed to be the primary precursor of the carbonaceous residue deposited on the spent sand. Thus the coking tendency of the bitumen-derived liquid during hydrotreating was expected to be less than that of the native bitumen. The production of the bitumen-derived hydrocarbon liquid from the Whiterocks tar sand has been

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described in detail by Sung[10].

Hydrotreater Process Unit

Process studies were conducted in a fixed bed reactor which operated in the upflow mode to minimize thermal gradients in the catalyst bed and to ensure complete wetting of the catalyst. Constant withdrawal of the liquid product from the high pressure separator permitted continuous operation of the system. Operating problems associated with the high pressure separator and liquid level controller required that both liquid and gaseous products be withdrawn from the system through the back pressure control valve. A schematic of the hydrotreater system is presented in Figure 1. A schematic of the reactor is presented in Figure 2.

The reactor was machined from 316 stainless steel and was designed for operation at a maximum pressure of 34.5 MPa at 773 K; however, the maximum operating pressure was limited to 20.7 MPa at 773 K. Manifold valves on the inlet and outlet lines from the reactor permitted operation in either the upflow or downflow mode. An exotherm was observed in the inlet region of the catalyst bed where the highly reactive olefins in the bitumen-derived liquid hydrogenated. The catalyst was diluted with quartz sand (50% by volume) in the inlet region of the bed (~20%) to trim the exotherm. A typical reactor temperature profile is presented in Figure 3. The denitrogenation and desulfurization data were correlated using the kinetic average
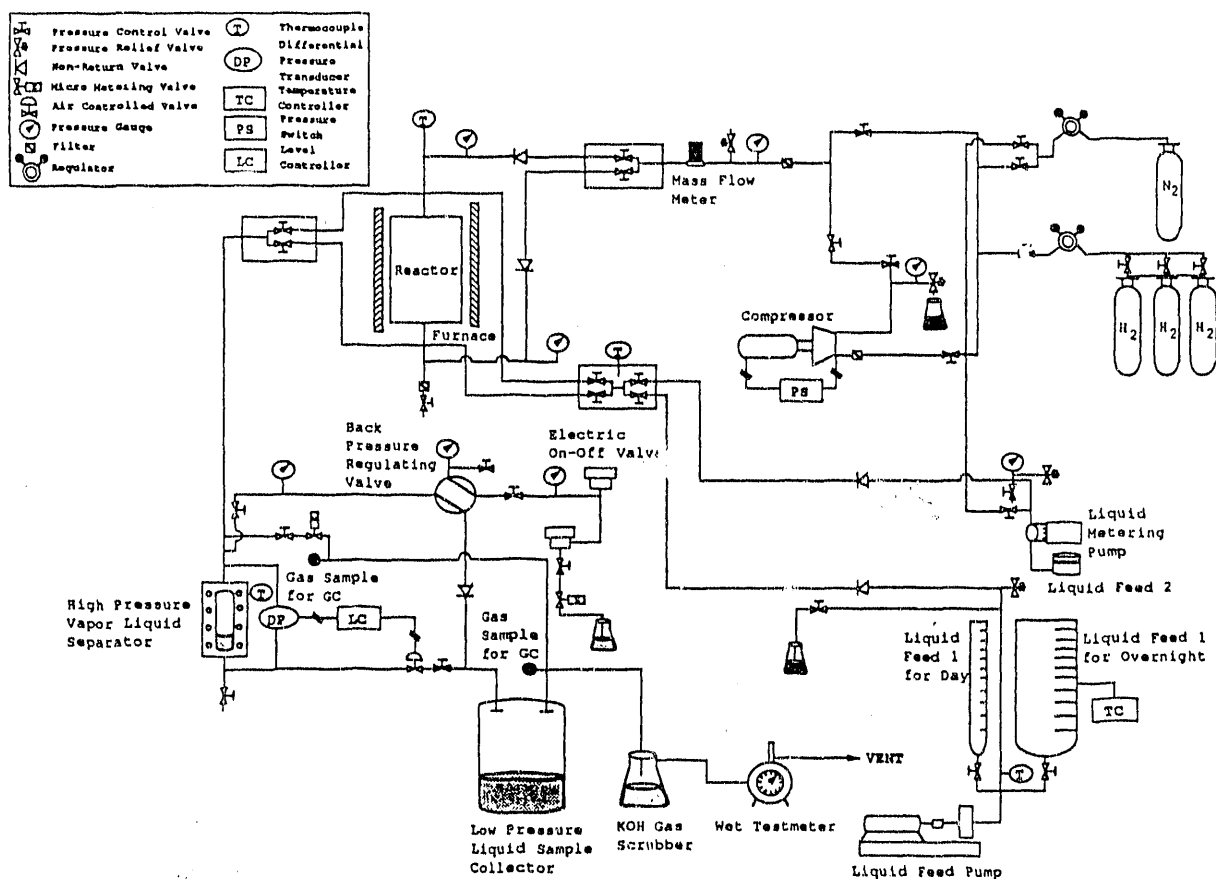

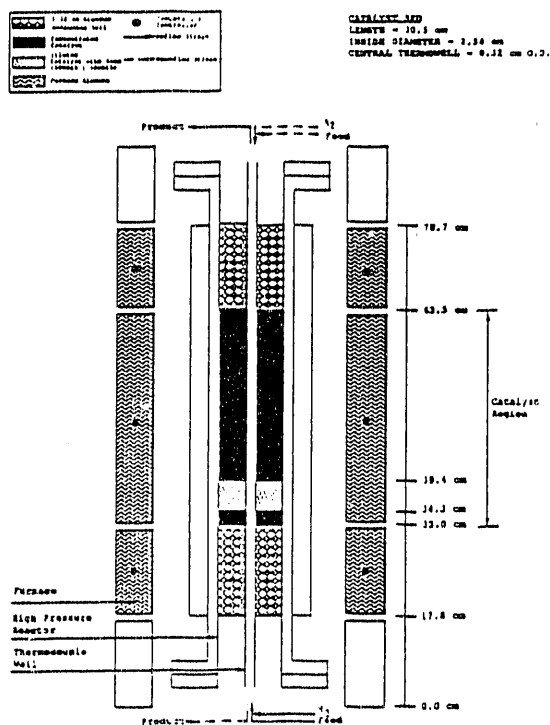**Figure 1.** Flow Diagram of the Hydrotreating Catalyst Testing Unit

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Figure 2. Reactor Schematic

Figure 3: Reactor Temperature Profile for Upflow Operation

temperature, T_k, which was, defined as follows:

$$T_k - \int_a^b \exp\left[\frac{-E_a}{RT(x)}\right]dx \qquad (1)$$

where E_a is the apparent activation energy and $T(x)$ is an appropriate function which describes the variation of the catalyst bed temperature as a function of axial distance, x, in the bed. The kinetic average temperature calculated from Equation 1 for the temperature profile presented in Figure 3 was 663 K. The arithmetic average temperature was also 663 K. The kinetic average temperature and the arithmetic average temperature never differed by more than 0.5°C due to the dilution of the catalyst bed and to operation in the upflow mode.

The base case operating conditions for the hydrotreating study were as follows: reaction temperature, 619 K (653 °F); liquid hourly space velocity (LHSV), 0.5 h^{-1}; total reactor-pressure, 13.7 MPa (1980 psia) and hydrogen-to-hydrocarbon feed ratio, 890 m^3/m^3 (5000 scf/bbl). The API gravity of the total liquid product was constant at 23.2 °API after the reactor had been on-stream for 94 hours at the base case conditions. At this point, it was assumed that the catalyst had attained a stationary state and that 95% of the coke deposition had occurred. Once the reactor system had attained the stationary state, it was allowed to operate on automatic control overnight. A series of experiments were conducted in which the system was operated in a cyclic mode (base case condition/desired reaction condition/base case
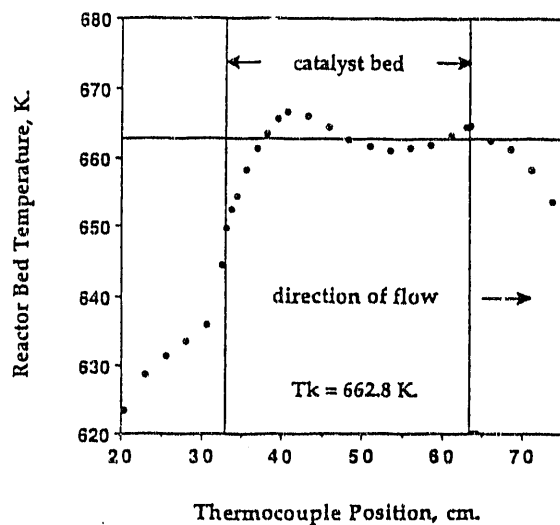
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condition) for approximately 800 hours. The total liquid product from each experiment was collected for analyses. The analytical test procedures conformed to those outlined in the ASTM manuals.

Mass balances were taken for approximately 3 hours at the end of a 16-hour line-out period after the system had attained a stationary state at the new reaction conditions. The mass balances were conducted by monitoring the liquid fed to the reactor system for discrete time periods. Liquid samples were collected at room temperature and gas samples were collected at 76 K (in a container immersed in a liquid nitrogen bath) during the material balance. At the conclusion of each mass balance the gas condensate and liquid samples were weighed and the gas condensate was weathered into a vapor collector and analyzed by gas chromatography. All the mass balances were greater than 97.5 wt%. The design, construction and operation of the hydrotreater system has been discussed in detail by Longstaff[11].

The extent of nitrogen removal was the key reactivity parameter followed during the course of the study; however, the key operating parameter followed on the catalyst testing unit during the run was the specific and/or API gravity of the total liquid product. The nitrogen content of the total liquid product is plotted as a function of API gravity in Figure 4. The nitrogen-gravity data reported by Sullivan and Stangeland[12] for shale oil hydrodenitrogenation is also plotted in Figure 4. The similarity between the trends indicated that the nitrogen-gravity correlation for the hydrodenitrogenation of the bitumen-derived liquid could be used with confidence. Thus, the nitrogen-
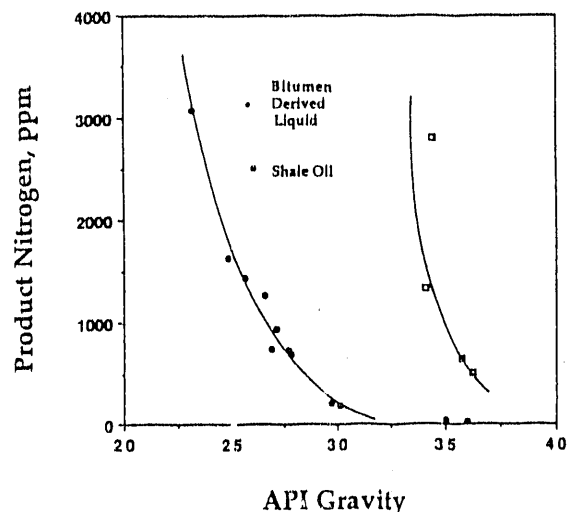

Figure 4: Nitrogen Concentration - API Gravity Correlation

gravity correlation was presumed to be acceptable as an on-line guide to estimate the real time influence of changes in operating variables during the course of the study.

Catalyst and Catalyst Activation

A total of 136 cm³ of a UNOCAL 1/16" quadralobe $Ni/Mo/Al_2O_3$ hydrodenitrogenation (HDN) catalyst was placed in the middle section (30.5 cm long) of the reactor. The catalyst was mixed with Ottawa sand in the inlet region of catalyst bed to dissipate the global heat of reaction generated by the olefin hydrogenation reactions. The catalyst contained 3.3 wt.% NiO, 12.8 wt% MoO_3, and 0.8 wt% P_2O_5. It had a surface area of 241 m^2/g and a pore volume (Hg porosimetry) of 0.55 cm^3/g. The sulfiding conditions were specified by the catalyst manufacturer. A solution of dimethyl disulfide in kerosene (~ 2 wt% sulfur) was used to sulfide the catalyst at a LHSV of 1.0 h^{-1}. The hydrogen-to-sulfiding solution ratio was 890 m^3/m^3 (5000 scf/bbl). The catalyst was contacted with the sulfiding solution at the ambient temperature and the temperature was increased to 505 K (450°F) at a rate

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of 28°C per hour. The catalyst was held at 505 K for 2 hours or until sulfur breakthrough was observed. The temperature was then raised to 644 K (700°F) at a rate of 28°C per hour. The catalyst was held an additional 2 hours at 644 K to complete the sulfiding step. The sulfiding solution was discontinued and the reactor temperature was adjusted to the initial run temperature.

RESULTS AND DISCUSSION

Process Variable Study

The primary process variables investigated were the reaction temperature, the total reactor pressure and the liquid hourly space velocity. The operating conditions at which the process variable data were obtained are presented in Figure 5 and are summarized as a function of time on-stream in Table 2. Each experiment was conducted by changing one variable at a time from the base case conditions. Three sets of experimental data were obtained at the following conditions: 1) the reaction temperature was varied at constant pressure (13.7 MPa [1980 psig]) and LHSV (0.5 h^{-1}); 2) the LHSV was varied at constant temperature (663 K [733°F]); and pressure (13.7 MPa) and 3) the total pressure was varied at constant temperature (663 K) and LHSV (0.5 h^{-1}). The hydrogen-to-bitumen-derived liquid ratio was the same in all experiments (890 m^3/m^3 [5000 scf/bbl]). The experiments were conducted in a random manner to avoid systematic errors. After the stationary state was attained and a material balance was completed a second experiment was conducted at the base case conditions listed in Table 3.

Table 2

Run Conditions Employed to Hydrotreat
Bitumen-Derived Liquid from Whiterocks
Tar Sand Formation

Run Number	Time On Stream (h)	Reaction[a] Temperature (K)	LHSV (h^{-1})	Reactor[b] Pressure (MPa)
6	96	617.	0.50	13.7
7	117	681.	0.51	13.7
8	145	617.	0.54	13.6
9	170	663.	0.50	13.7
10	188	618.	0.49	13.7
11	262	663.	0.20	13.7
12	285	619.	0.48	13.8
13	309	664.	0.48	17.1
14	334	6'8.	0.51	13.5
15	359	665.	0.50	11.0
16	383	619.	0.50	13.7
17	429	663.	0.35	13.7
18	454	664.	0.37	13.6
19	477	618.	0.52	13.7
20	505	662.	0.50	15.5
21	524	617.	0.49	13.6
22	548	644.	0.49	13.6
23	581	618.	0.49	13.7
24	601	663.	0.77	13.8
25	623	618.	0.52	13.6
26	648	680.	0.19	13.5

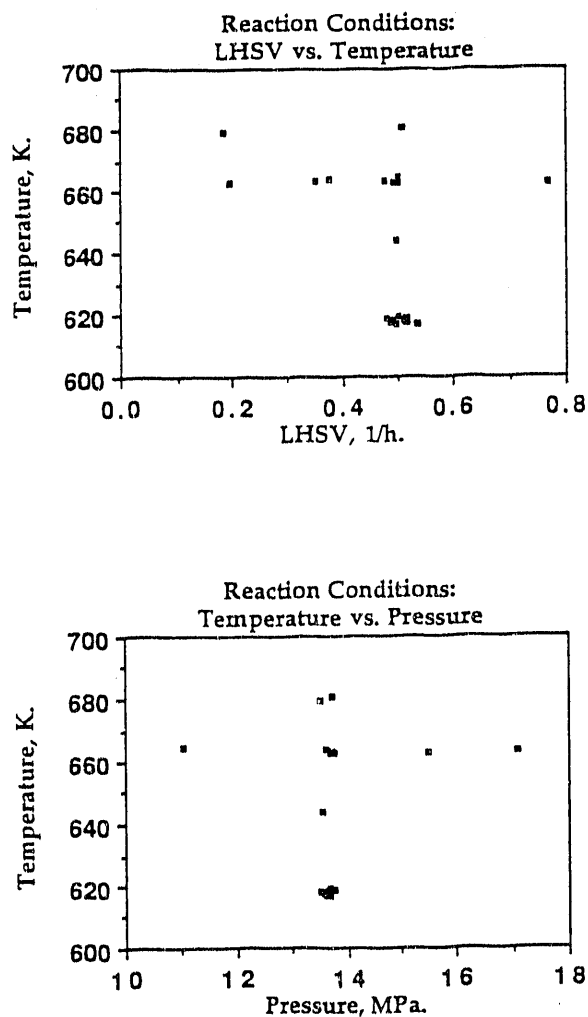[a] Average catalyst bed temperature
[b] Reactor outlet pressure

Figure 5: Reaction Conditions

Table 1

Operating Conditions for Hydrotreating
the Bitumen-Derived Liquid from the Whiterocks
Tar Sand Deposit

Process Variables Operating Ranges	
Temperature, K (°F)	616-680 (650-765)
LHSV, h⁻¹	0.185-0.77
Pressure, MPa (psia)	11.0-16.9 (1600-2450)
H₂/Oil Ratio, m³/m³ (SCF/B)	890 (5000)
Catalyst⁰	
Loading, cm³	136
Surface Area, m²/g	241
Pore Volume⁰, cm³/g	0.53
Composition	
NiO, wt%	3.3
MoO₃, wt%	12.5
P₂O₅, wt%	0.8
Base Process Conditions	
Temperature, K (°F)	616 (651)
Reactor Pressure, MPa (psia)	13.6 (1980)
LHSV, h⁻¹	0.50
H2/Oil Ratio, m³/m³ (SCF/B)	890 (5000)

⁰ UNOCAL 1/16 "Quadralobe HDN Catalyst
⁰ Hg porosimetry

The API gravity of the total liquid product produced at the base case operating conditions is plotted as a function of time on-stream in Figure 6. The reactor was operated continuously at the base case conditions for the first 100 hours on-stream. The API gravity of the liquid produced in the initial deactivation period (~ 100 hours on-stream) was monitored; however, those points were not plotted so that the change in API gravity at the base case conditions during the course of the process variable study could be clearly discerned. It should be

T = 618.2 K.
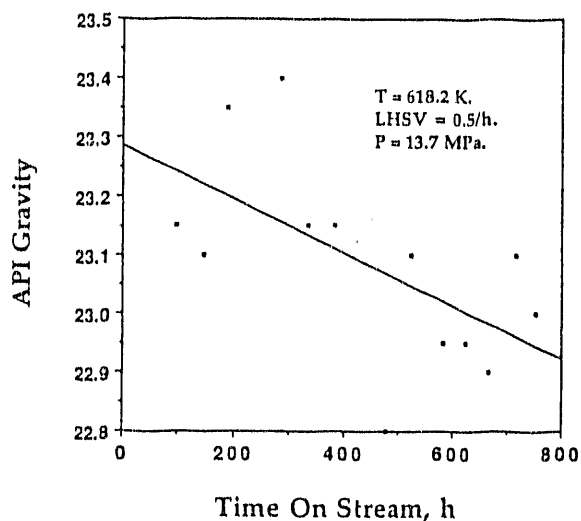LHSV = 0.5/h.
P = 13.7 MPa.

Time On Stream, h

Figure 6: API Gravity vs Time On-Stream for Base Case Runs

noted that the spread of the points above and below the least squares fit is accentuated by the expansion of the y-axis to a range of 0.7 of a degree of API. The difficulty associated with exact reproduction of the temperature and space velocity in the base case experiments also contributed to the scatter of the data. The deactivation or aging rate was estimated to be 0.25°F/day over approximately 800 hours on-stream. The deactivation rate was somewhat higher than expected; however, this was likely due to the nature of the feedstock. Furthermore, it should be noted that the study was not intended to precisely determine the aging rate of the catalyst. A portion of the accelerated deactivation was attributed to the variation in operating conditions from experiment to experiment.

Effect of Reaction Temperature

The effect of reaction temperature at a fixed pressure and space velocity on the product distribution and yields is presented in Figures 7 and 8 and in Table 4 and on denitrogenation in Table 4. All experiments were conducted at a reactor pressure of 13.7 MPa, a space velocity of 0.5 h⁻¹ and a H₂-to-hydrocarbon ratio of 890 m³/m³. As the average catalyst temperature increased, a significant increase in the API gravity of the total liquid product relative to the bitumen-derived liquid was observed; that is, 29.8 °API and 18.5°API, respectively, at a reaction temperature of 681 K. The API gravity of the total liquid product increased from 23.2 to 29.8 °API as the reaction temperature increased from 619 to 681 K. The increase in API gravity as a function of temperature was accompanied by an increase in H₂ consumption and in the atomic H/C ratio of the total liquid product as expected. The physical
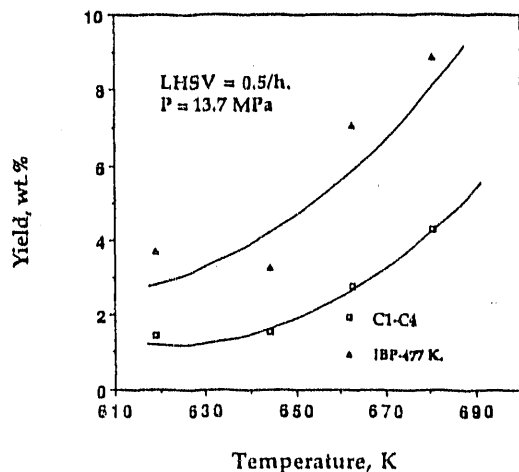
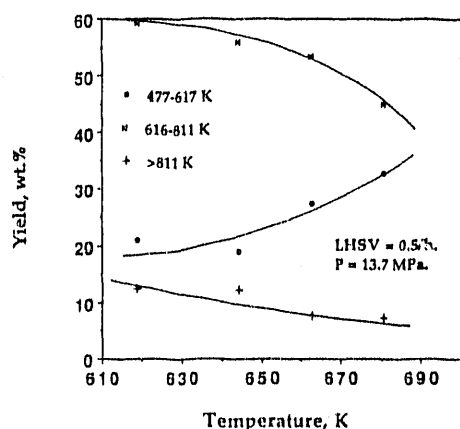Figure 7: Effect of Reactor Temperature on Light Gas and Naphtha Yields

Figure 8: Effect of Reactor Temperature on Middle Distillate Gas Oil and Resid Yields

Table 4

Effect of Temperature on the Product Properties of the
Hydrotreated Bitumen-Derived Liquid from
Whiterocks Tar Sand Formation

Run Number	16	22	9	7
Process Operating Conditions				
Temperature, K	619	644	661	681
LHSV, h⁻¹	0.5	0.5	0.5	0.5
Residence Time, h	1.0	2.0	2.0	2.0
Pressure, MPa	13.7	13.6	13.7	13.7
API Gravity	23.2	24.9	26.3	29.1
Specific Gravity	0.915	0.905	0.891	0.878
H_2 Cons., m^3/m^3	147	166	182	195
(SCF/bbl)	(825)	(933)	(1019)	(1097)
Elemental Analysis				
C, wt%	87.5	87.6	87.3	87.2
H, wt%	12.2	12.2	12.6	12.5
Nitrogen, ppm	1070	1631	744	202
Sulfur, ppm	271	65	45	16
H/C Atomic Ratio	1.66	1.66	1.72	1.76
Product Yields, wt%				
C_1	0.2	0.2	0.3	0.3
C_2	0.3	0.3	0.4	0.3
C_3	0.4	0.4	0.3	1.3
i-Butane	0.2	0.2	0.3	0.4
n-Butane	0.4	0.4	0.6	0.3
C_5^+ Liquid Product	97.4	98.3	96.3	94.3
Liquid Yield Vol.%	99.3	101.4	100.5	100.3
Simulated Distillation of Total Liquid Product				
Volatility, wt%	87.5	87.7	92.3	92.3
IBP, K	423	429	396	395
IBP-477 K	3.7	3.2	7.1	3.3
477-617 K	20.9	19.3	27.4	32.3
617-811 K	59.2	62.3	53.3	45.1
>811 K	12.5	12.3	7.7	7.2

and chemical properties of the total liquid product did not change significantly as the temperature increased from 619 to 644 K; however, there was a substantial reduction in the nitrogen and sulfur concentrations. The nitrogen content decreased by 47% and the sulfur content decreased by 76%. Above 644 K the decrease in sulfur and nitrogen contents were accompanied by significant changes in the physical and chemical properties of the total liquid product (Table 4). These changes were presumed to be related to the conversion of more refractory heteroatom species. This speculation was confirmed by the product distribution data plotted in Figures 7 and 8. The resid (> 811 K) and gas oil (617-811 K) yields declined as the temperature increased while the middle distillate, (477-617 K), naphtha (IBP - 477 K) and C_1-C_4 gas yields increased. The shifts in boiling range and molecular weight were related to the conversion of more refractory compounds at higher temperatures. Although higher temperatures would have led to higher denitrogenation activity, 681 K was selected as the upper reaction temperature limit to suppress thermal cracking and excessive coke deposition.

Effect of LHSV   The effect of LHSV on product distribution and yields at a fixed reaction temperature and pressure is presented in Figures 9 and 10 and in Table 5 and on denitrogenation in Table 5. The space velocity experiments were conducted at a reactor pressure of 13.7 MPa, a temperature of 663 K, and a H_2-to-hydrocarbon ratio of 890 m^3/m^3.

As the liquid hourly space velocity decreased the API gravity of the hydrotreated total liquid product relative to the bitumen-derived
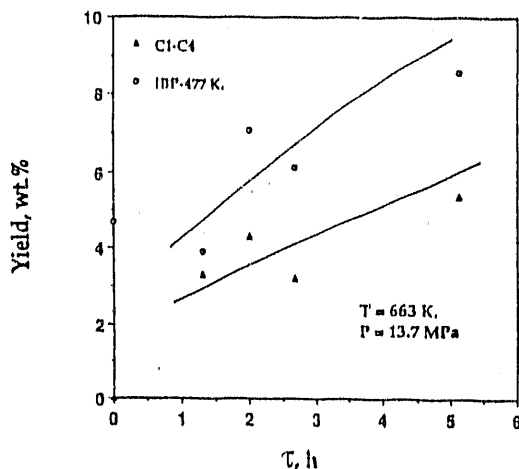
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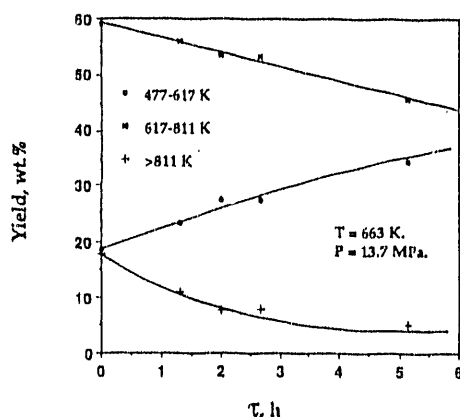Figure 9: Effect of Space Velocity on Light Gas and Naphtha Yields

Figure 10: Effect of Space Velocity on Middle Distillate, Gas Oil and Resid Yield

Table 5

Effect of LHSV on the Product Properties of the
Hydrocracked Bitumen-Derived Liquid from
Whiterocks Tar Sand Formation

Run Number	24	9	13	11
Process Operating Conditions				
LHSV, h⁻¹	0.77	0.5	0.37	0.2
τ, h	1.3	2.0	2.7	5.1
Temperature, K	663	663	664	663
Pressure, MPa	13.9	13.7	13.6	13.7
API Gravity	25.7	26.9	27.3	30.2
Specific Gravity	0.900	0.893	0.888	0.875
H₂ Cons., m³/m³	147	182	239	277
(SCF/bbl)	(825)	(1019)	(1341)	(1554)
Elemental Analysis				
C, wt%	87.4	87.1	87.2	87.0
H, wt%	12.4	12.6	12.7	13.0
Nitrogen, ppm	1434	748	686	186
Sulfur, ppm	149	45	77	18
H/C Atomic Ratio	1.69	1.72	1.75	1.78
Product Yields, wt%				
C₁	0.6	0.5	0.5	1.1
C₂	0.5	0.6	0.5	1.1
C₃	1.0	0.4	0.9	1.7
i-Butane	0.4	0.3	0.4	0.5
n-Butane	0.8	0.6	0.8	0.9
C₄⁺ Liquid Product	95.6	96.1	96.1	94.5
Liquid Yield, Vol.%	98.5	100.8	100.2	100.5
Simulated Distillation of Total Liquid Product				
Volatility, wt%	89.1	92.3	92.2	95.0
IBP, K	417	396	400	380
IBP, 477 K	1.9	7.1	4.1	4.5
477-617 K	23.3	27.4	27.3	34.3
617-811 K	56.0	53.3	53.1	45.4
> 811 K	10.9	7.7	7.3	5.0

liquid increased: 30.2 °API and 18.5°API, respectively, at a LHSV of 0.2 h⁻¹. The API gravity of the total liquid product increased from 25.7 to 30.2°API as the space velocity decreased from 0.77 to 0.2 h⁻¹. The increase in API gravity as space velocity decreased was accompanied by an increase in the hydrogen consumption and in the atomic H/C ratio of the total liquid product. The space velocity appeared to have a greater influence on hydrogen consumption than reaction temperature and was related to the higher C_1-C_4 yields as the space velocity decreased. The sulfur and nitrogen contents both decreased significantly as the space velocity decreased from 0.77 to 0.2 h-1. The sulfur content, 77 ppm, at a space velocity of 0.37 h⁻¹ (Table 5) may have been high due to inefficient stripping of dissolved H_2S prior to analysis.

The simulated distillation data (Table 5) indicated that more refractory, asphaltic compounds were converted at lower space velocities; that is, the residual and gas-oil fractions (>811 K and 617-811 K, respectively) decreased whereas, the middle distillate (477-617 K), naphtha (IBP-477 K) and C_1-C_4 gas yields increased (Figures 9 and 10). The heavy gas oil and residual fractions represented less than 50 % of the total liquid product produced at the lowest space velocity. This would translate to a reduced demand on the hydrocracker in downstream processing of this total liquid product or of its heavier fractions.

Effect of Reactor Pressure

The effect of reactor pressure at fixed space velocity and reaction temperature on product distribution and yields is presented in Table 6. The effect of pressure on hydrogen consumption is presented in Figure

11. The reaction temperature and LHSV were maintained at 663 K. and 0.5 h⁻¹, respectively, while the pressure varied from 11 to 17.1 MPa. The reactor pressure did not appear to exert a significant influence on the product distribution and yield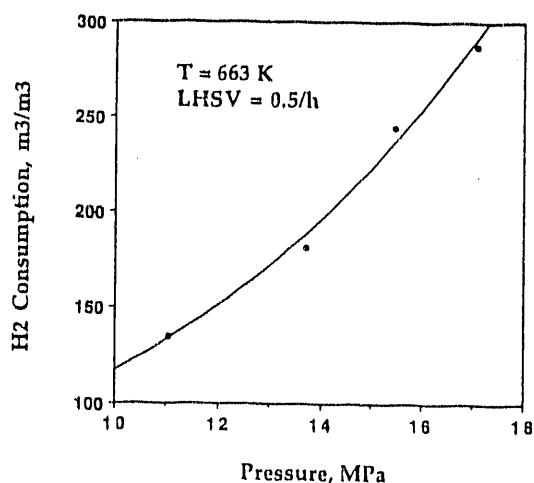s nor on the physical and chemical properties of the total liquid product (Table 6). The API gravity of the total liquid product increased from 26.6 to 27.7°API as the pressure increased from 11 to 17.1 MPa. The product distribution, as indicated by simulated distillation data, appeared to be independent of the reactor pressure in the range 11 to 17.1 MPa (Table 6). The nitrogen content of the total liquid product decreased with increased reactor pressure. The sulfur content did not vary significantly as the pressure increased from 11 to 17.1 MPa; however, the fractional sulfur conversion exceeded 0.69 over the entire range of pressures studied. The total liquid product produced at 15.5 MPa contained dissolved H_2S and NH_3 which had not been completely stripped from the sample prior to analysis. Thus, the reported nitrogen and sulfur contents were suspect. Pressure appeared to exert a significant influence on hydrogen consumption (Figure 11). Small increases in the total reactor pressure increased hydrogen consumption to a much greater extent than increasing the temperature or decreasing the LHSV.

Figure 11: Hydrogen Consumption versus Pressure

The nitrogen content of the total liquid product versus hydrogen consumption is presented in Figure 12 for three series of experiments in which the catalyst activity was adjusted by: 1) increasing the reaction temperature at fixed space velocity and reactor pressure; 2) by decreasing LHSV at fixed reaction temperature and reactor pressure; and 3) by increasing reactor pressure at fixed reaction temperature and space velocity. The relative effects of temperature, LHSV and pressure on hydrogen consumption are summarized in this figure. The nitrogen content-H_2 consumption curve obtained when temperature was varied had the steepest slope. Thus, large
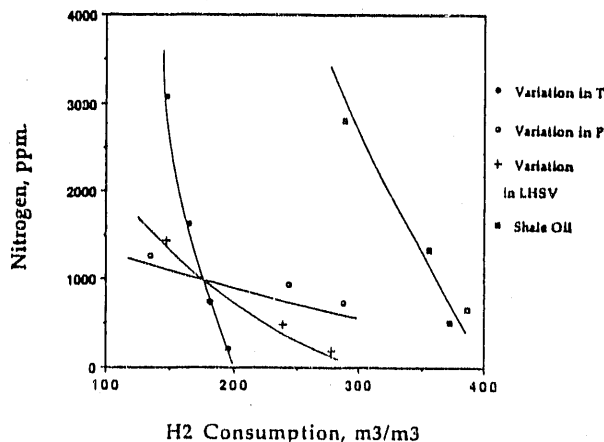
Table 6

Effect of System Pressure on the Product Properties of the Hydrocracked Bitumen-Derived Liquid From Whiterocks Tar Sands Formation

Run Number	15	9	20	13
Process Operating Conditions				
Pressure, MPa	11.0	13.7	15.5	17.1
Temperature, K	663	663	662	664
LHSV, h⁻¹	0.5	0.5	0.5	0.5
t, h	2.0	2.0	2.0	2.1
API Gravity	26.6	26.3	27.1	27.7
Specific Gravity	0.895	0.893	0.892	0.889
H_2 Con., m³/m³	135	182	244	287
(SCF/bbl)	(755)	(1019)	(1370)	(1611)
Elemental Analysis				
C, wt%	87.4	87.3	87.2	87.3
H, wt%	12.4	12.6	12.7	12.6
Nitrogen, ppm	1260	748	942	727
Sulfur, ppm	28	45	113	57
H/C Atomic Ratio	1.69	1.72	1.74	1.72
Product Yields, wt%				
C_1	1.0	0.5	0.3	1.0
C_2	1.1	0.5	0.7	1.0
C_3	1.6	0.3	1.2	1.1
i-Butane	0.3	0.3	0.4	0.3
n-Butane	0.5	0.6	0.3	0.5
C_5 Liquid Product	94.1	96.3	95.5	95.7
Liquid Yield, Vol.%	98.2	100.3	99.6	100.3
Simulated Distillation of Total Liquid Product				
Volatility, wt%	95.1	92.3	90.9	90.3
IBP, K	412	396	412	403
IBP-477 K	4.9	7.1	4.9	5.3
477-617 K	25.7	27.4	25.3	26.4
617-811 K	54.2	53.3	54.3	53.5
>811 K	9.2	7.7	9.1	9.2

Figure 12: Product Nitrogen vs. H₂ Consumption

Variation in T
Variation in P
Variation in LHSV
Shale Oil

Nitrogen, ppm.

H2 Consumption, m3/m3

decreases in nitrogen content were accompanied by small increases in hydrogen consumption. The opposite was observed for the nitrogen content-H_2 consumption curve obtained when pressure was varied: small decreases in product nitrogen content were accompanied by large increases in hydrogen consumption. The influence of LHSV on the slope of the nitrogen content-H_2 consumption curve was intermediate between the temperature and pressure trends.

If nitrogen removal were the sole objective in hydrotreating then nitrogen conversion could be accomplished at the lowest hydrogen consumption by operating at high temperatures. However, nitrogen removal is rarely the only objective in hydrotreating. For example, the aromatic contents of the jet fuel and diesel fractions must meet specifications; thus, a specific level of hydrogen consumption is required to saturate aromatic moieties. Even though high operating temperatures removed more nitrogen than operating at high hydrogen pressure, high operating temperatures led to greater gas yields and more rapid catalyst deactivation.

It was interesting to note that significant conversion of the resid fraction was accomplished at high temperatures and fixed space velocity and/or at long reactor residence times and fixed reaction temperature. The feed contained 18 wt.% resid (defined as material boiling above >811 K.) and the liquid produced at the highest temperature (681 K, 0.5 LHSV, 13.7 Mpa.) contained 6 wt.% resid. This represented 65% conversion of the residual fraction to lower boiling materials.

Statistical Analysis

The reaction conditions, product properties and yield structure of each run were analyzed by multivariate statistical analysis to determine the effect of temperature, LHSV and pressure on the product properties. It was found that the yields were most significantly affected by the reactor temperature. LHSV was also important, but to a lesser extent than temperature. Reactor pressure had only a minor influence on product yields and conversions.

Pyrolysis-Hydrotreating Process Sequence

The changes which occurred in the processing sequence tar sand pyrolysis followed by hydrotreating of the bitumen-derived liquid are illustrated in Table 7 in which selected physical and chemical properties of the native bitumen, the bitumen-derived liquid and the hydrotreated total liquid product are presented. The bitumen-derived liquid was produced at ambient pressure, a feed sand retention time of 17.2 minutes and a sweep gas flow rate of 2.2 SCMH. The pyrolysis zone temperature ranged from 773 to 813 K. The hydrotreated total liquid product was produced at a reactor pressure of

Table 7

Properties of Bitumen and Bitumen-Derived Liquids
from the Whiterocks Deposit Tar Sand

	Native Bitumen	Bitumen-Derived Liquid	Hydrotreated Bitumen-Derived Liquid
Operating Conditions			
Temperature, K	--	773-813	680
Pressure, MPa	--	0.088	13.7
Feed Sand Retention			
Time, min	--	17.2	--
LHSV, h⁻¹	--	--	0.185
H_2-to-Hydrocarbon Ratio, m^3/m^3	--	--	890.
API			
Gravity	11.7	18.5	35
Conradson Carbon,			
Residue wt%	8.1	4.7	NA
Pour Point, K	336	279	259
Simulated Distillation			
Volatility, wt%	40.5	82.2	97.
IBP K	489	414	370
IBP - 477 K, wt%	0.0	4.7	12.5
477 - 617 K, wt%	4.7	18.5	40
617 - 811 K, wt%	35.6	59.0	34.7
>811 K, wt%	59.5	17.8	2.5
Elemental Analysis			
C, wt%	85.1	86.0	86.7
H, wt%	12.3	11.1	13.3
N, wt%/ppm	1.2	1.1	43 ppm
S, wt%/ppm	0.4	0.3	16 ppm
O, wt%	1.1	1.5	0.
Ni, ppm	67	9	NA
V, ppm	<5	<1	NA
Atomic H/C Ratio	1.73	1.55	1.84

13.7 MPa (1980 psia), an average catalyst bed temperature of 680 K (764 F) a liquid hourly space velocity of 0.19 h⁻¹ and a H_2-to-hydrocarbon feed ratio of 890 m^3/m^3 (5000 scf/bbl).

The pyrolysis or coking step resulted in three important changes that had an impact on the hydrotreater: a reduction in the Conradson carbon residue; 8.1 to 4.7 wt %; a reduction in the metals content of the total liquid product relative to the native bitumen, 67 ppm Ni to 9 ppm Ni; and a decrease in the residual fraction (>811 K) from 59.5 wt% to 17.8 wt%. These changes led to the selection of a hydrodenitrogenation (HDN) catalyst for the hydrotreater studies rather than a hydrodemetallation (HDM) catalyst. The reduction in boiling range did not lead to a concomitant reduction in the nitrogen and sulfur contents of the bitumen-derived liquid relative to the native bitumen; however, there was a reduction in the hydrogen content.

The hydrotreating step resulted in a reduction of the nitrogen content from 1.1 wt% for the bitumen-derived liquid to 43 ppm for the hydrotreated total liquid product. A similar reduction in the sulfur content was observed: 0.32 wt% to 16 ppm, respectively. These reductions were accompanied by a significant increase in hydrogen content: 11.1 wt% to 13.3 wt%. The boiling range and molecular weight reductions were significant in that 40% of the total liquid product was in the high density, high energy aviation turbine fuel boiling range, 477-617 K(400-650°F). Fractional distillation of the total liquid product produced a water-white aviation turbine fuel fraction. The 617 K plus hydrotreated liquid product would make an excellent fluid catalytic cracker or fuels hydrocracker feedstock.

Preliminary Process Kinetics

A secondary objective of this study was to determine the apparent kinetic parameters for the following rate expressions:

$$r_N = k_{HDN} C_N^a P_{H_2}^b \qquad (2)$$

$$r_S = k_{HDS} C_S^c P_{H_2}^d \qquad (3)$$

where k_{HDN} is the apparent rate constant for hydrodenitrogenation, k_{HDS} is the apparent rate constant for hydrodesulfurization; P_{H_2} is the partial pressure of hydrogen; C_N is the concentration of organic nitrogen; and C_S is the concentration of organic sulfur.

The kinetics of nitrogen and sulfur removal were lumped due to the complexity of the feed; that is, the

bitumen-derived liquid contained a broad range of nitrogen and sulfur compounds which differed in the ease of conversion and/or heteroatom removal.

Neither the denitrogenation nor the desulfurization data could be successfully organized according to a first order dependence in nitrogen or sulfur heteroatom concentration. That is, the plots of the logrithms of the fraction unconverted as a function of inverse space velocity were non-linear.

The integrated kinetic equation for hydrodenitrogenation was given by

$$k_N \tau = f(x_N) \qquad (4)$$

The function $f(x_N)$ was given by

$$f(x_N) = \frac{1}{c_{No}^{(n-1)}} \frac{1}{(n-1)} [(1-x_N)^{(1-n)} -1]$$

.... (5)

where τ is the contact time or reciprocal of the space velocity, h; X_N is the conversion of nitrogen, and C_{No} is the initial concentration of nitrogen, wt%. The rate constant, k_N, incorporated the hydrogen concentration term which was assumed to be approximately constant at high H_2-to-hydrocarbon ratios; that is,

$$k_N = k_{HDN} P_H^b \qquad (6)$$

A plot of the function $f(x_N)$ versus the inverse of the space velocity should give a straight line of slope k_N; however, this procedures required a value for the order with respect to nitrogen removal, n. Various values of n, the order for nitrogen removal,

were chosen and $f(x_N)$ was plotted as a function of the reciprocal of the LHSV to obtain a family of curves. The value of n which gave the best fit of the data to a straight line was the apparent reaction rate order for nitrogen removal. The denitrogenation order for the bitumen-derived liquid was determined to be 1.55 from the slope of the plot in Figure 13.
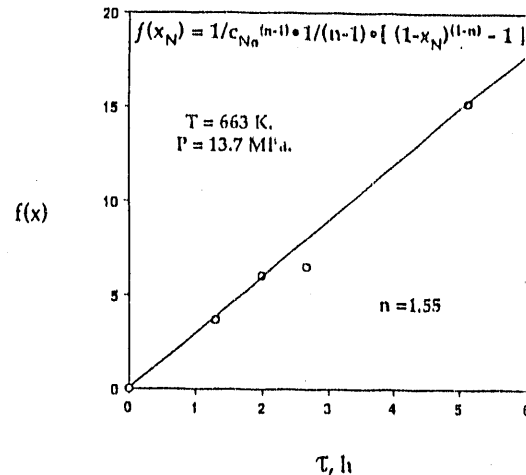

Figure 13: Integrated Rate Expression, f(x_N), as a Function of Residence Time

Kinetic studies of model nitrogen compounds have shown that hydro-denitrogenation is first order with respect to nitrogen[13]. The 1.55 order reported here was explained on the basis of the broad spectrum of nitrogen containing species present in the bitumen-derived liquid. It was presumed that nitrogen removal proceeded by a set of competitive parallel, first order reactions. The overall order for a reaction network of this type was expected to be between 1 and 2[14]. The greater than first order dependence on the fraction of unconverted nitrogen was contrary to the first order dependence reported for Paraho shale oil[12] and for an atmospheric residuum (>514 K (> 465°F))[14]. The difference is of interest in that the Safaniya residuum and the whole shale oil

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contained 0.24 and 2.18 wt.% nitrogen, respectively, whereas the bitumen-derived liquid contained 1.1 wt.%. Thus, it was expected that denitrogenation of the bitumen-derived liquid would also have been first order in nitrogen concentration. We presumed that the difference in order was related to the differences in the nature of the nitrogen compounds in the bitumen-derived liquid relative to the shale oil and the Safaniya residuum.

The same procedure was used to determine the order for sulfur removal which was 1.5. The sulfur order is consistent with that reported by Riley [14] for hydrodesulfurization of the Safaniya atmospheric residuum. The greater than first order dependence for hydrosulfurization has previously been explained by considering the overall kinetics as a sum of competing, parallel first order reactions[14-16].

The activation energy for nitrogen removal was obtained from the slope of the Arrhenius plot for denitrogenation (Figure 14). There appeared to be a distinct break in the curve and two values for the apparent activation energy. At low temperatures where less refractory nitrogen compounds reacted the activation energy was 75.3 kJ/mol (18 kcal/mol). At high temperatures where the more refractory nitrogen compounds were expected to react the activation energy was 184.1 kJ/mol (44 kcal/mol). It was presumed that the change in the apparent activation energy was also related to the complex nature of the collection of nitrogen compounds in the bitumen-derived liquid. The Arrhenius plot for hydrodesulfurization is presented in Figure 15. The activation energy calculated from the slope was 92.1
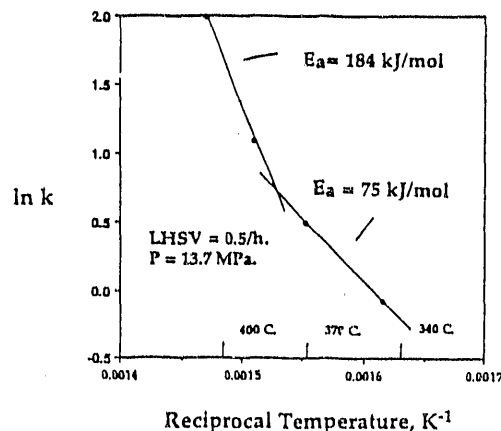

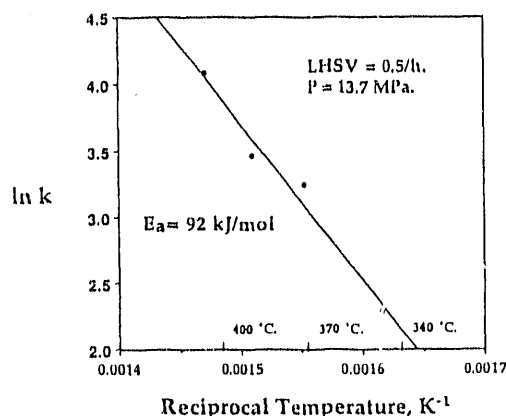Figure 14: Arrhenius Plot for Denitrogenation of Bitumen-Derived Liquid

Figure 15: Arrhenius Plot for Desulfurization of Bitumen-Derived Liquid

kJ/mol (22 kcal/mol) and was constant throughout the range of temperatures studied.

The effect of reactor pressure on denitrogenation and desulfurization was examined; however, the scatter in the data when $\ln(k \cdot p^a_{Total})$ was plotted versus $\ln(p_{Total})$ was quite large, thus, it was not possible to organize the data in a satisfactory manner. The effect of hydrogen consumption on nitrogen conversion for the bitumen-derived liquid at fixed space velocity and pressure as the temperature varied from 619 to 681 K is presented in Figure 16. The data reported by Sullivan and Stangeland
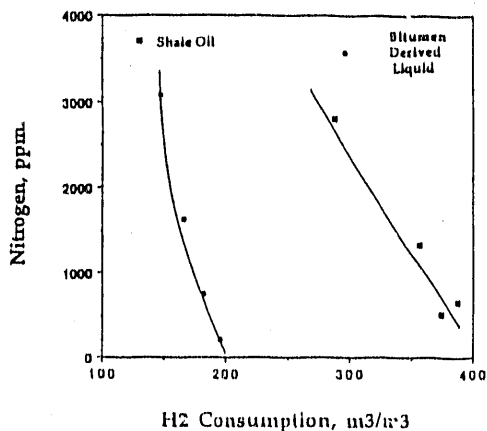
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H2 Consumption, m3/m3

Figure 16: Denitrogenation vs. H₂ Consumption for Shale Oil and Bitumen-Derived Liquid

(12) for hydrodenitrogenation of shale oil is also presented in Figure 16 for comparison. The hydrogen consumption during hydrodenitrogena-tion of the bitumen-derived liquid was about half the hydrogen consump-tion for hydrodenitrogenation of shale oil. This difference was presumed to be related to the lower nitrogen content of the bitumen-derived liquid, 1.12 wt%, which was half the concentration of shale oil; however, the slopes of the plots were quite similar.

CONCLUSIONS

The processing sequence tar sand pyrolysis followed by hydro-treating appeared to be a viable concept by which the Whiterocks tar sand resource could be exploited. The 477-617 K (400-650°F) boiling range fraction of the hydrotreated bitumen-derived liquid would be an excellent candidate for high-density aviation fuels. Catalyst activity during the hydrotreating of Whiterocks bitumen-derived liquid remained stable during 800 hours of operation and should remain reasonab-ly stable for longer periods. The catalyst deactivation rate was 0.14°C/day (0.25°F/day). The reactivity of the bitumen-derived liquid was similar to the reactivity of shale oil.

The apparent reaction orders were 1.55 and 1.5 for nitrogen and sulfur removal, respectively. These fractional orders suggested the occurrence of many parallel first order reactions, each with a different first order rate constant. The activation energy for denitrogen-ation was 75.3 kJ/mol (18 kcal/mol) at lower conversions and temperatures where less refractory nitrogen-contained species reacted. At higher temperatures and conversions where the more refractory species reacted the activation energy was 184.1 kJ/mol (44 kcal/mol). The activation energy for desulfurization was 92.1 kJ/mol (22 kcal/mol) over the range of temperatures studied.

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Appendix: Derivation of the Integrated form of the Rate Equations

The rates of hydrodenitrogenation and/or hydrodesulfurization reactions were given by equations of the form

$$r_i = k_i C_H^m C_i^n \qquad \text{(A-1)}$$

where k_i is the intrinsic rate constant for denitrogenation or desulfurization and C_i the concentration of the nitrogen or sulfur heteroatomic species. If the H_2-to-hydrocarbon ratio was sufficiently high and the reaction temperature was sufficiently low then C_H was assumed to be constant such that

$$k_{APP,i} = k_i C_H^m \qquad \text{(A-2)}$$

Thus, the rate expression reduced to a pseudo nth order equation in C_i; that is

$$r_i = k_{APP,i} C_i^n \qquad \text{(A-3)}$$

If we restrict consideration to denitrogenation then the equation was given by

$$r_N = k_{APP,N} C_N^n \qquad \text{(A-4)}$$

If the rate of denitrogenation is expressed as

$$r_N = -\frac{dC_N}{d\tau} \qquad \text{(A-5)}$$

where τ is the liquid phase residence time (1/LHSV) and the concentration, C_N, is expressed as

$$C_N = C_{N,o}(1-X_N) \qquad \text{(A-6)}$$

Upon substitution into the rate expression we obtain the following equation

$$C_{N,o} \frac{d(1-X_N)}{d\tau} = k_{APP,N} C_{N,o}^n (1-X_N)^n \qquad \text{(A-7)}$$

Upon rearrangement the following equation was obtained

$$\int \frac{dX_N}{(1-X_N)^n} = \int k_{APP,N} C_{N,o}^{n-1} d\tau \qquad \text{(A-8)}$$

The integrated kinetic equation was

$$k_{APP,N}\tau = \frac{1}{C_{N,o}^{n-1}} \frac{1}{n-1}\left[(1-X_N)^{(1-n)}-1\right] \qquad \text{(A-9)}$$

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