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HYDROTREATING THE BITUMEN FROM THE WHITEROCKS OIL SAND DEPOSIT

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Abstract

The bitumen from the Whiterocks oil sand deposit in the Uinta Basin of eastern Utah was hydrotreated in a fixed-bed reactor to determine the extent of upgrading as a function of process operating variables. The process variables investigated included reactor pressure (11.2-16.7 MPa); reactor temperature (641-712 K) and liquid hourly space velocity (0.19-0.77 h^{-1}). The hydrogen/oil ratio, 890 m^3 m^{-3}, was fixed in all experiments. A sulphided Ni-Mo on alumina hydrodenitrogenation catalyst was used in these studies.

The deactivation of the catalyst, 0.2 °C/day, was monitored by the decline in the API gravity of the total liquid product with time on-stream at a standard set of conditions. The effect of temperature, WHSV, and pressure on denitrogenation, desulphurization, and metals removal were studied and apparent kinetic parameters determined. The effect of process variables on residuum conversion and Conradson carbon residue reduction were also investigated.

Introduction

The exploitation of Utah's oil sands will occur by a combination of *in situ* thermal enhanced oil recovery and mining-surface recovery techniques. The mining-surface recovery processes include aqueous separation[1,2], pyrolysis[3,4] and solvent extraction[5-7]. The separation and extraction processes produce the bitumen which can be used as an asphalt base stock[8,9]. The pyrolysis processes produce a bitumen-derived liquid which can be used as a refinery feedstock[10,11]. The high nitrogen content of the Uinta Basin bitumens and the bitumen-derived liquids (0.8-1.2%)[12] indicated that hydrotreating would be required as a primary upgrading process. Bitumen recovered by toluene extraction of Whiterocks oil sand was used as the hydrotreater feedstock in this study.

Drum size quantities of the crushed and screened ore were collected and toluene extracted to obtain toluene/bitumen solutions. The toluene/bitumen solutions were concentrated by rotary evaporation and batch distillation to produce a bitumen feed which contained <0.1 wt% toluene. The physical and chemical properties of the bitumen are presented in Table 1[13].

Gravity (API)	11.4
Density (288.7 K) (g cm^{-1})	0.989
Pour point, K	330
Pentane insolubles	5.0
Simulated distillation	
Volatility (wt%)	43.3
IBP, K	489
477-617 K (wt%)	6.3
617-811 K (wt%)	37.0
>811 K (wt%)	56.7
Elemental Analysis	
C (wt%)	85.9
H (wt%)	11.1
N (wt%)	1.07
S (wt%)	0.37
Atomic H/C ratio	1.54

Table 1. Analysis of the bitumen from the Whiterocks oil sand deposit

The objective of this investigation was to conduct a process-variable study related to the hydrotreating of the bitumen with particular emphasis on denitrogenation. The process variables studied included

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[1] To whom inquiries should be directed

the reactor temperature, the total reactor pressure, the weight hourly space velocity, and the hydrogen partial pressure.

Experimental Methods and Means

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 by means of an Annin valve permitted continuous operation of the system. A simplified schematic of the hydrotreater system is presented in Figure 1. The denitrogenation and desulphurization data were correlated using the kinetic average temperature, T_k, which was defined as follows:

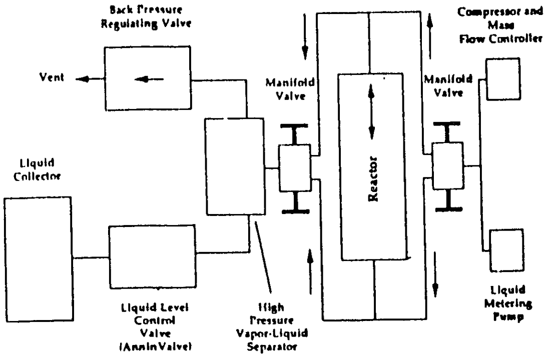

Figure 1. Simplified flow diagram of the hydrotreating catalyst testing unit

$$T_k = \frac{\left(-\frac{E_a}{R}\right)}{\ln\left[\frac{1}{L}\int_0^L \exp\left[-\frac{E_a}{RT(x)}\right]dx\right]} \qquad (1)$$

where E_a is the 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 base case operating conditions for the hydrotreating study were as follows: reactor temperature, 642 K (696 °F); weight hourly space velocity, 0.75 h^{-1}; total reactor pressure, 13.7 MPa and hydrogen-to-oil feed ratio, 890 m^3 m^{-3} (5000 scf/bbl). The API gravity of the total liquid product was constant between 15.5-15.7 °API after the reactor had been on-stream for 100 h at the base case conditions. At this point it was assumed that the catalyst had attained a stationary state. A series of experiments were conducted in which the system was operated in a cyclic mode (base-case conditions/desired condition/base-case condition) for approximately 700 h. 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 h 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 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 vapour collector and analyzed by gas chromatography. All the mass balances were greater than 97.5 %. The design, construction and operation of the hydrotreater system have been discussed in detail by Longstaff[3].

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 gravity 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 2. The nitrogen-gravity data reported by Longstaff[13] for hydrotreatment of bitumen-derived liquid obtained by fluidized-bed pyrolysis of Whiterocks oil sand are also included in Figure 2, as well as data reported by Sullivan and Stangeland[14] for shale oil hydrotreating. The similarity between the trends indicated that the

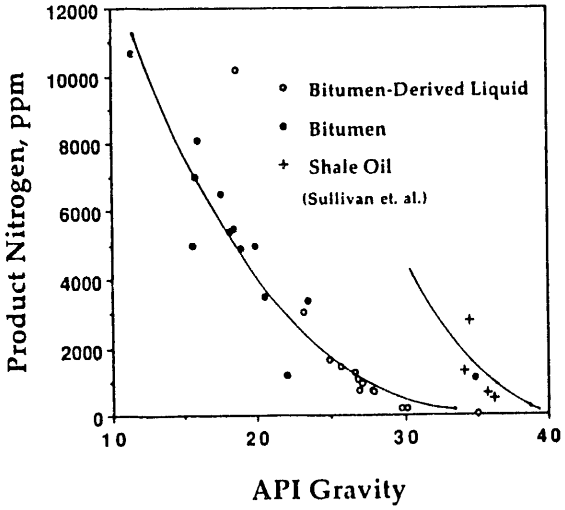

Figure 2. Nitrogen concentration versus API gravity

nitrogen-gravity correlation for the hydrodenitrogenation (HDN) of the bitumen could be used with confidence. Thus, the nitrogen-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.

The difference in bitumen-derived liquid and bitumen reactivities are illustrated in Figure 2. Although the bitumen-derived liquid data was obtained under the same sets of conditions as the bitumen data, the hydrotreated bitumen-derived liquid samples are clustered at lower product nitrogen levels than the hydrotreated bitumen samples. Clearly, the bitumen nitrogen is more refractory than the bitumen-derived liquid nitrogen. The difference is most likely due to the higher molecular weight of the bitumen.

Catalyst and Catalyst Activation. A total of 152 cm^3 of a UNOCAL 1/16" quadralobe Ni/Mo/Al$_2$O$_3$ HDN catalyst was placed in the middle section (30.5 cm long) of the reactor. The catalyst contained 3.3 wt% NiO, 12.8 wt% MoO$_3$ and 0.8 wt% P$_2$O$_5$. It had a surface area of 241 m^2 g^{-1} and a pore volume (Hg porosimetry) of 0.55 cm^3 g^{-1}. The sulphiding conditions were specified by the catalyst manufacturer. A solution of dimethyl disulphide in kerosene (~2 wt% sulphur) was used to sulphide the catalyst at an LHSV of 1.0 h^{-1}. The hydrogen-to-sulphiding solution ratio was 890 m^3 m^{-3} (5000 scf/bbl). The catalyst was contacted with the sulphiding solution at the ambient temperature and the temperature was increased to 505 K (450 °F) at a rate of 28 °C h^{-1}. The catalyst was held at 505 K for 2 h or until sulphur breakthrough was observed. The temperature was then raised to 664 K (700 °F) at a rate of 28 °C h^{-1}. The catalyst was held an additional 2 h at 644 K (700 °F) to complete the sulphiding step. The sulphiding 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 weight hourly space velocity. The operating conditions at which the process-variable data were obtained are presented in Figure 3 and are summarized in Table 2. Each experiment was conducted by changing one variable at a time from the base 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 psia)) and WHSV (0.75 h^{-1}); (2) the WHSV was varied at constant temperature (664 K (735 °F)) and pressure (13.7 MPa); and (3) the total pressure was varied at constant temperature (664 K) and WHSV (0.75 $^{-1}$). The hydrogen-to-bitumen ratio was 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.

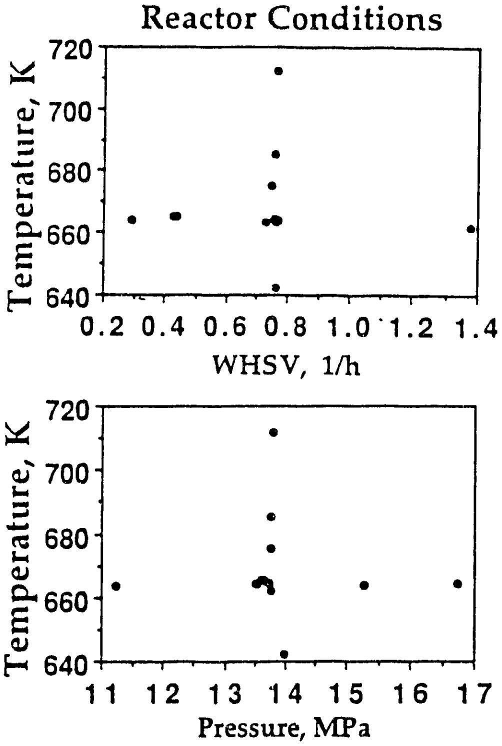

Figure 3. Reaction conditions: WHSV versus temperature at fixed pressure; temperature versus pressure at fixed WHSV

Run number	Time on stream (h)	Reaction temperature (K)	WHSV (h^{-1})	Reactor pressure (MPa)
5	98	642	0.67	13.7
6	122	685	0.75	13.7
7	141	642	0.75	13.6
8	165	664	0.76	13.6
9	193	642	0.76	14.0
10	239	664	0.29	13.5
11	261	642	0.75	13.6
12	284	664	0.76	16.7
13	312	642	0.73	13.6
14	335	663	0.76	11.2
15	363	642	0.74	13.7
16	407	665	0.43	13.7
17	415	642	0.76	13.5
18	437	643	0.79	13.5
19	461	664	0.73	15.3
20	485	642	0.77	13.7
21	513	675	0.74	13.8
22	539	642	0.75	13.8
23	559	662	1.38	13.7
24	582	643	0.76	13.7
25	605	665	0.76	13.7
26	629	642	0.74	13.7
27	664	665	0.43	13.6
28	692	643	0.77	13.7
29	713	712	0.76	13.8
30	735	642	0.71	13.6

Table 2. Run conditions employed to hydrotreat bitumen from the Whiterocks oil sand deposit

The API gravity of the total liquid product produced at the base-case operating conditions is plotted as a as a function of time on-stream in Figure 4. It should be 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 0.4 °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 0.20 °C day^{-1} over approximately 700 h on-stream. The deactivation rate was similar to the deactivation rate obtained by processing bitumen-derived liquid obtained from pyrolysis of Whiterocks oil sand[13]. Even though bitumen contains three times as much residuum as bitumen-derived liquid the deactivation rates were similar. This is attributed to the presence of 2-3 ppm arsenic in the Whiterocks bitumen-derived liquid and the Whiterocks bitumen.

Process variables operating ranges	
Temperature (K (°F))	642-711 (696-822)
Pressure (MPa (psia))	11.2-16.9 (1626-2426)
WHSV (h^{-1})	0.29-1.38
LHSV (h^{-1})	0.18-0.86
H_2/oil ratio (m^3 m^{-3} (scf/bbl)	890 (5000)
Catalyst[a]	
Loading (cm^3)	152
Surface area (m^2 g^{-1})	241
Pore Volume[b] (cm^3 g^{-1})	0.55
Composition (wt%)	
NiO	3.3
MoO_3	12.8
P_2O_5	0.8
Base Process Conditions	
Temperature (K (°F))	642 (696)
Pressure (MPa (psia))	3.7 (1980)
WHSV (h^{-1})	0.75
LHSV (h^{-1})	0.45

[a] UNOCAL 1/16" quadralobe
[b] Hg porosimetry

Table 3. Operating conditions for hydrotreating the Whiterocks bitumen

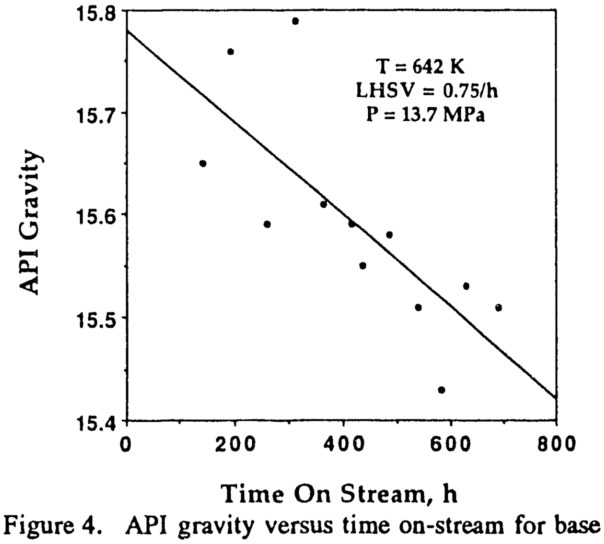

Figure 4. API gravity versus time on-stream for base case runs

Prior to the last base-case run, the reactor was operated at 712 K (Run 29) in order to determine the extent of molecular weight reduction which could be achieved at high temperatures. Although substantial molecular weight reduction occurred; when the catalyst was returned to the base-case conditions there was a significant increase in the specific gravity of the base-case produced liquid relative to liquid samples produced during previous base-case runs. It was concluded that semi-continuous catalyst replacement would be necessary for high temperature hydrotreating of bitumen.

Preliminary Process Kinetics. The rates of sulphur, nitrogen and residuum conversion may be fit by power rate law kinetics:

$$r_i = k_i C_i^a P_{H_2}^\beta \qquad (2)$$

When a significant fraction of the heteroatoms or the residuum are present in unreactive fractions such as asphaltenes, the kinetics of their conversion can be expressed as the result of two parallel first order reactions. The fraction unconverted for any component j, which consists of a reactive or facile fraction and a less reactive or refractory fraction is given by Equation 3:

$$\frac{C_j}{C_{j,o}} = x_A \exp[-k_A \tau] + (1-x_A)\exp[-k_B \tau] \qquad (3)$$

where x_A is the fraction of component j which is facile, τ is the reciprocal WHSV, and k_A and k_B are the first order rate constants for the facile and refractory fractions of component j.

Effect of WHSV. The effect of WHSV on the conversion of nitrogen, sulphur and residuum is plotted in Figures 5-7 and is summarized in Table 4. Figure 5 indicates that nitrogen conversion occurred according to pseudo-first order kinetics with a rate constant of 0.6 h^{-1}. The negative natural log of unconverted sulphur with respect to reciprocal WHSV is plotted in Figure 6. The data gave a straight line which had a y-intercept greater than zero. This indicates that sulphur conversion data can be described by two parallel reactions according to Equation 3. The rate constants for facile and refractory sulphur conversion were 4.8 h^{-1} and 0.5 h^{-1}, respectively, and that 35% of the bitumen sulphur is refractory, which represents 0.12 wt% of the total bitumen feed. This in agreement with data reported by Riley[16] and Ohtsuka[17]. Figure 7 is similar in appearance to Figure 6 indicating that residuum also consists of facile and refractory fractions. In Figure 7 the data at the highest reciprocal WHSV suggests that residuum conversion goes through a maximum. This is not the case, but rather is an artifact resulting from insufficient line-out time between Run 9 and Run 10. The first order rate constants for facile and refractory residuum conversion were determined to be 3.8 h^{-1} and 0.25 h^{-1}, respectively. Furthermore, the data indicated that 62% of the residuum was refractory, which represents 35% of the total bitumen. The dotted lines in Figures 6 and 7 are the least-squares fit using the values of k_A, k_B and x_A reported here for sulphur and residuum. Like sulphur, residuum has also been reported to consist of facile and refractory fractions[18].

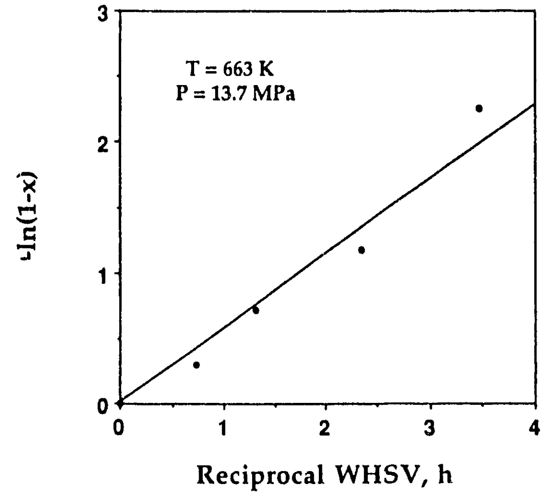

Figure 5. Plot of -ln(1-x) versus reciprocal WHSV for nitrogen conversion

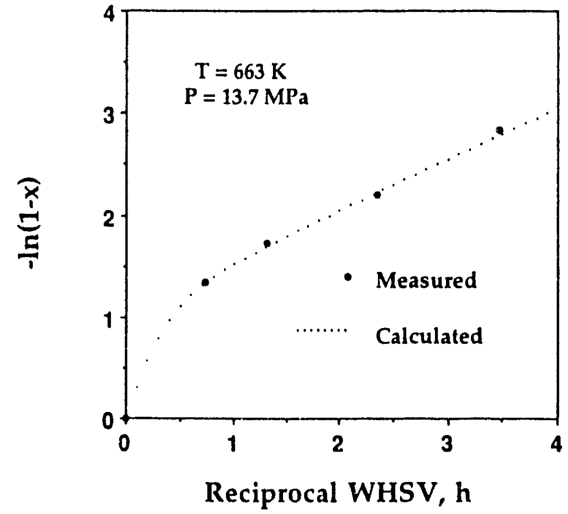

Figure 6. Plot of -ln(1-x) versus reciprocal WHSV for sulphur conversion

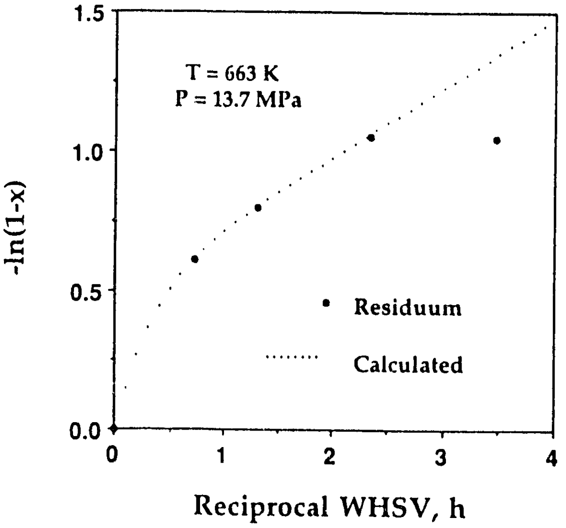

Figure 7. Plot of -ln(1-x) versus reciprocal WHSV for residuum conversion

Run number	23	8	16	10
Process operating conditions				
WHSV (h^{-1})	1.38	0.76	0.43	0.29
τ (h)	0.73	1.31	2.34	3.47
Temperature (K)	662	664	665	664
Pressure (MPa)	13.7	13.5	13.7	13.5
API Gravity	16.0	18.1	20.5	22.0
Specific Gravity(g cm^{-3})	0.955	0.938	0.920	0.909
Elemental analysis				
C (wt%)	86.0	86.1	86.3	86.1
H (wt%)	11.7	11.9	12.3	12.4
Nitrogen (ppm)	8100	5400	3500	1200
Sulphur (ppm)	980	680	430	230
H/C atomic ratio	1.62	1.65	1.70	1.72
Product yields (wt%)				
C_1	0.3	0.3	0.4	0.8
C_2	0.2	0.2	0.2	0.5
C_3	0.3	0.3	0.4	0.3
i-Butane	0.1	0.1	0.1	0.3
n-Butane	0.2	0.2	0.2	0.5
C_4^+ liquid product	99.1	97.6	95.7	95.3
Liquid yield (vol%)	101.2	101.5	101.0	101.7
Simulated distillation of total liquid product				
Volatility (wt%)	68.9	73.8	79.3	79.2
C_5^+ -477 K (wt%)	4.1	4.0	4.6	6.0
477-617 K (wt%)	13.9	16.5	20.7	21.2
617-811 K (wt%)	50.9	53.2	54.0	51.3
>811 K (wt%)	31.1	26.2	20.7	20.8

Table 4. Effect of WHSV on the product properties of the hydrotreated bitumen from the Whiterocks oil sand formation

The chemical nature of refractory sulphur is suggested from the linking of sulphur and residuum conversion kinetics which inferred that refractory sulphur consisted of organic sulphur present in high molecular weight unreactive moieties which crack slowly. Thus, residuum conversion was presumed to be the rate determining step for refractory sulphur conversion. It has been suggested that refractory sulphur is the sulphur present in asphaltenes.[16,17] However, this is an unsatisfactory explanation for Whiterocks bitumen because less than 7% of the Whiterocks bitumen sulphur is asphaltenic.[19] Since asphaltenes are a continuum of functionalities present in lower molecular weight species[20,21] the refractory nature of asphaltenic sulphur and the refractory Whiterocks sulphur probably both result from steric constraints of high molecular weight species, rather than from the polarity of refractory sulphur compounds. This is in agreement with work by Trytten and co-workers[22] who reported over an order of magnitude difference between the intrinsic rate constants for nitrogen and sulphur conversion as the feed average molecular weight is increased from 200 to 450 g mol^{-1}.

Effect of Reaction Temperature. The effect of reaction temperature at a fixed pressure and WHSV on the conversion of nitrogen, sulphur and residuum is presented in Figures 8-10 and in Table 5. All experiments were conducted at a WHSV of 0.76 h^{-1} and a pressure of 13.7 MPa. The natural log of the first order rate constants for the refractory sulphur and residuum fractions are plotted in Figures 8 and 9. The apparent activation energy for refractory sulphur conversion, 146 kJ mol^{-1}, is similar in magnitude to the apparent E_a for refractory residuum conversion, 134 kJ mol^{-1}, which supports the contention that refractory residuum conversion is the rate limiting step for refractory sulphur conversion.

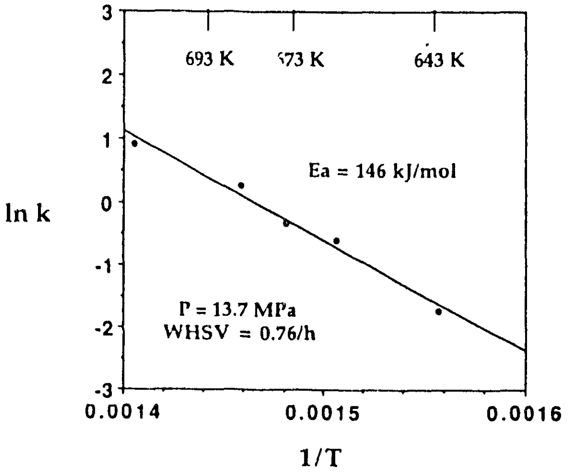

Figure 8. Arrhenius plot for desulphurization

In Figure 9 the natural log of the first order rate constant for the whole residuum conversion is also plotted and shows that there are two types of conversion for residuum: a lower temperature region where facile residuum conversion occurs and a higher temperature region where the facile residuum is presumably totally converted. The low apparent activation energy for residuum conversion at the lower temperature suggests that facile residuum conversion consists of diffusionally hindered catalytic hydrocracking of reactive functionalities in the residuum fraction. Refractory residuum conversion probably consists of thermal cracking of the refractory portion of residuum. Activation energies of 230 kJ mol^{-1} for residuum mild hydrocracking in ebulliated beds have been reported[23]. The difference may be related to differences in reactor scale and configuration.

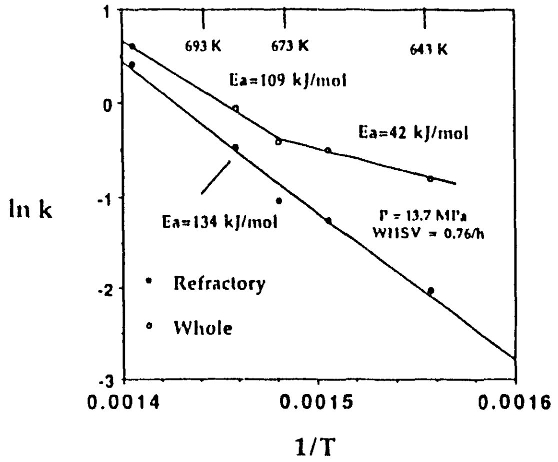

Figure 9. Arrhenius plot for conversion of refractory and whole residuum

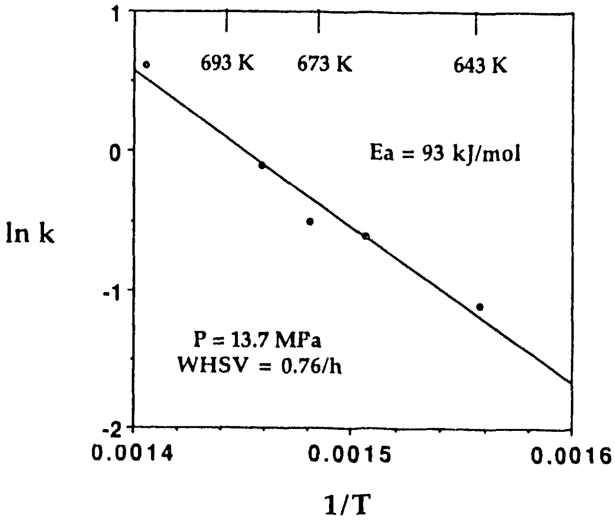

Figure 10. Arrhenius plot for denitrogenation

The natural log of the first order rate constant for nitrogen conversion is plotted versus reciprocal temperature in Figure 10. The slope gave an activation energy of 93 kJ mol^{-1} for denitrogenation, which compares with values of denitrogenation activation energies of 121 kJ mol^{-1} reported for coker gas oil (723-773 K)[22].

Effect of Pressure. The effect of reactor pressure at fixed space velocity and reaction temperature on product distribution and yields is presented in Table 6. The reaction temperature and WHSV were held constant at 663 K and 0.76 h^{-1}, respectively, while the pressure varied from 11.2 to 16.7 MPa. The reaction order with respect to hydrogen partial pressure, β, for nitrogen, refractory sulphur and refractory residuum conversion were determined to be 0.7, 0 and 0 respectively. The higher value of β for denitrogenation is indicative of the greater importance that hydrogen plays in denitrogenation[24]. The similar effect of hydrogen partial pressure on refractory sulphur and residuum conversion again confirms that refractory sulphur conversion is linked to residuum conversion and not to hydrogenation of aromatic rings.

Run number	9	8	21	6	29
Process operating conditions					
Temperature (K)	642	664	675	685	712
WHSV (h^{-1})	0.76	0.76	0.74	0.75	0.76
τ (h)	1.32	1.31	1.35	1.32	1.32
Pressure (MPa)	14.0	13.5	13.8	13.7	13.8
API Gravity	15.8	18.1	19.9	23.4	34.8
Specific Gravity	0.956	0.939	0.925	0.898	0.811
Elemental analysis					
C (wt%)	85.9	86.1	86.2	86.1	86.1
H (wt%)	11.7	11.9	12.1	11.9	12.7
Nitrogen (ppm)	7000	5400	5000	3400	1100
Sulphur (ppm)	1100	680	530	250	50
H/C atomic ratio	1.62	1.65	1.63	1.65	1.76
Product yields (wt%)					
C_1	0.1	0.3	0.6	0.9	2.1
C_2	0.1	0.2	0.4	0.6	1.6
C_3	0.1	0.3	0.5	0.9	2.8
i-Butane	0.04	0.1	0.2	0.9	1.2
n-Butane	0.1	0.2	0.4	0.6	2.2
C_5^+ liquid product	99.0	97.7	97.4	97.5	89.3
Liquid yield (vol%)	101.7	101.5	102.0	103.5	98.7
Simulated distillation of total liquid product					
Volatility (wt%)	68.4	73.8	76.2	83.4	94.5
C_5^+ -477 K (wt%)	1.0	4.0	5.6	6.2	26.1
477-617 K (wt%)	12.6	16.5	19.8	25.0	40.6
617-811 K (wt%)	54.8	53.2	50.8	52.2	27.7
>811 K (wt%)	31.6	26.2	23.8	16.5	5.5

Table 5. Effect of temperature on the product properties of the hydrotreated bitumen from Whiterocks oil sand formation

Run number	14	8	19	12
Process operating conditions				
Pressure (MPa)	11.2	13.5	15.3	16.7
Temperature (K)	663	664	664	664
WHSV (h^{-1})	0.76	0.76	0.73	0.76
τ (h)	1.31	1.31	1.38	1.32
API Gravity	17.5	18.1	18.3	18.8
Specific Gravity	0.943	0.938	0.937	0.933
Elemental analysis				
C (wt%)	86.1	86.1	86.1	86.2
H (wt%)	11.9	11.9	12.0	12.1
Nitrogen (ppm)	6500	5400	5500	4900
Sulphur (ppm)	620	680	610	580
H/C atomic ratio	1.64	1.65	1.67	1.67
Product yields (wt%)				
C_1	0.1	0.3	0.1	0.3
C_2	0.04	0.2	0.05	0.2
C_3	0.1	0.3	0.1	0.3
i-Butane	0.02	0.1	0.03	0.1
n-Butane	0.04	0.2	0.05	0.2
C_5^+ liquid product	96.0	97.6	97.1	98.6
Liquid yield (vol%)	100.	101.5	101.6	103.2
Simulated distillation of total liquid product				
Volatility (wt%)	72.9	73.8	73.5	73.9
C_5^+ -477 K (wt%)	3.6	4.0	3.6	.3.7
477-617 K (wt%)	16.3	16.5	16.5	16.4
617-811 K (wt%)	53.1	53.2	53.3	53.8
>811 K (wt%)	27.1	26.2	26.5	26.1

Table 6. Effect of pressure on the product properties of the hydrotreated bitumen from the Whiterocks oil sand formation

Molecular Weight Reduction Modelling. Although denitrogenation was the main objective of Whiterocks bitumen hydrotreating, significant levels of boiling range reduction were observed. Boiling range reduction was modelled according to the model suggested by Mosby et. al.[18] which was used to predict boiling range yields in industrial hydrocrackers. A diagram of this network is presented in Figure 11 and accounts for conversion of facile and refractory residuum as well as virgin and cracked gas oil to lighter fractions. This model requires fourteen rate constants and it has been reported by Beaton et. al.[23] that all fourteen are necessary for satisfactory prediction of distillate fractions yields. This model may be simplified to contain only eleven rate constants by treating product and gas oils as a single lump.

Equations relating the yield of gas (C_1-C_4), naphtha (C_5-477 K), distillate (477-617 K), gas oil (617-811 K) and residuum (>811 K) were derived[13] and rate constants and activation energies were determined using software employing the multidimensional simplex method[25]. Values of rate constants and activation energies are presented in Table 7. The yields of gas, naphtha, distillate, gas oil and residuum with respect to reciprocal WHSV are plotted in Figure 12. The dotted

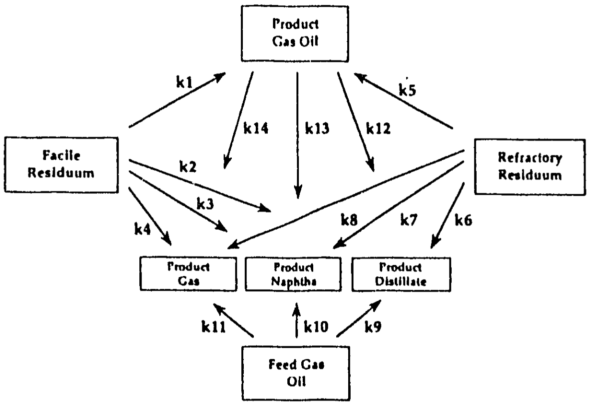

Figure 11. Diagram of reaction network used to model residuum and gas oil conversion

i	k_i (h^{-1})	$E_{a,i}$ (kJ mol^{-1})	$A_{o,i}$ (h^{-1})
1	2.51	3	1.2×10^{0}
2	1.09	36	8.0×10^{2}
3	0.50	39	5.7×10^{2}
4	0.01	33	4.3×10^{0}
5	0.22	155	3.3×10^{11}
6	0.00	69	3.3×10^{1}
7	0.00	80	8.3×10^{2}
8	0.005	296	9.3×10^{20}
9	0.10	187	4.8×10^{13}
10	0.003	7	1.1×10^{-2}
11	0.025	189	1.9×10^{13}
12	0.00	128	4.1×10^{6}
13	0.05	227	2.1×10^{0}
14	0.002	107	4.7×10^{5}

Table 7. Values of rate constants, activation energies and preexponential factor derived for the Mosby model

line represents the calculated yields of each fraction based on the kinetic data presented in Table 7. The yields of gas, naphtha, distillate, gas oil and residuum with respect to temperature are plotted in Figure 13. The dotted line represents the calculated yields of each fraction based on the kinetic data presented in Table 7. Because low conversions of bitumen were avoided, rate con-stants and activation energies should not be used to draw meaningful conclusions about facile residuum conversion. Since 24 data points were employed to determine fourteen rate constants, values reported in Table 7 are unsuitable for extrapolation.

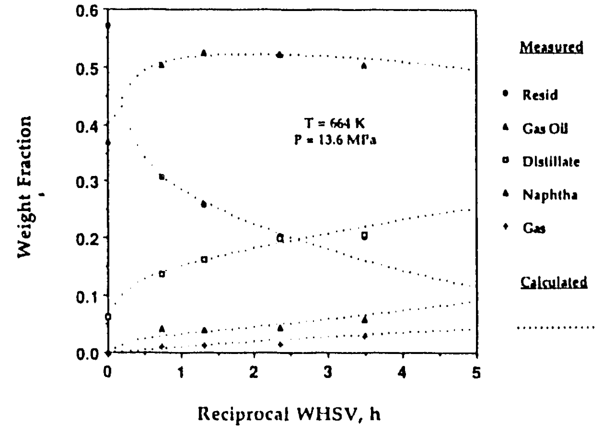

Figure 12. The effect of reciprocal WHSV on the calculated and measured yields of residuum and distillate fractions

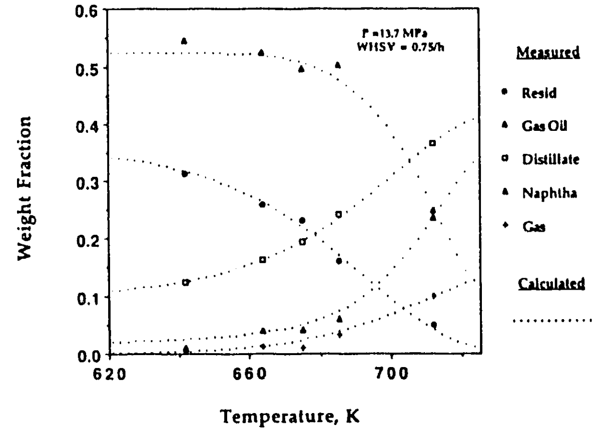

Figure 13. The effect of temperature on the calculated and measured yields of distillate fractions

Conclusions

Although substantial denitrogenation occurred during hydrotreating, the nitrogen levels in feed bitumen were so high that the nitrogen levels in the hydrotreated liquid product remained high. Substantial molecular weight reduction occurred during hydrotreating which was the result of thermal and catalytic cracking. Catalyst activity remained stable for over 700 h during normal hydrotreating conditions, but was substantially reduced after processing bitumen for short times at high temperatures.

Denitrogenation was pseudo-first order, while desulphurization and residuum conversion were represented by two parallel first order reactions. Sulphur conversion is linked to residuum conversion because sulphur contained in residuum moieties is unreactive until those moieties are cracked. The activation energy for denitrogenation was 93 kJ mol^{-1}. The activation energy for refractory sulphur conversion was 146 kJ mol^{-1} and was 134 kJ mol^{-1} for refractory residuum conversion.

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