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HYDROCRACKING OF ATHABASCA BITUMEN: EFFECT OF COAL-BASE CATALYST ON PILOT PLANT **OPERATION**

C.P. Khulbe, B.B. Pruden and J.M. Denis

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HYDROCRACKING OF ATHABASCA BITUMEN: EFFECT OF COAL-BASE CATALYST ON PILOT PLANT OPERATION

Ъy

C.P. Khulbe*, B.B. Pruden* and J.M. Denis**

ABSTRACT

In this study, pilot plant experiments are described in which a coal-base catalyst, consisting of a "coke getter" (high volatile A coal) coated with a desulphurization catalyst (Co-Mo-alumina, 15 wt % of the coal), was used in the hydrocracking of Athabasca bitumen. The slurry of bitumen and 2% coal-base catalyst was pumped into the bottom of a 4.5-& reactor (3.8 cm dia and 4 m long) at 460°C and 13.89 MPa pressure.

Pilot plant operation was smooth with a system pressure drop of less than 0.4 MPa. After 21 days of operation, the hot separator, preheaters and all transfer lines were clean but the reactor contained a hard porous deposit along 3 m of its length. Although hydrogen consumption in this run was higher than for a similar run without catalyst, there was more coke deposition. The probable cause of increased reactor coking was the low melting point of the coal which resulted in high ash content in the reactor fluid.

Sulphur removal was higher than for a run under similar conditions without additive. There were no problems with the additional hydrogen sulphide gas in the system.

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L'HYDROCRAQUAGE DE BITUME DE L'ATHABASCA: L'EFFET D'UN CATALYSEUR A BASE DE HOUILLE SUR LE FONCTIONNEMENT D'UNE INSTALLATION PILOTE

par

C.P. Khulbe*, B.B. Pruden* et J.M. Denis**

SOMMAIRE

La présente étude porte sur des essais qui ont été effectués sur une installation pilote et qui traitaient de l'hydrocraquage de bitume de l'Athabasca à l'aide d'un catalyseur à base de houille comprenant un getter à coke (un type de houille A très volatil) enduit d'un catalyseur désulfurant (alumine-Co-Mo, 15% de la houille, en poids). La boue de bitume et 2% du catalyseur à base de houille a été pompée au fond d'un réacteur de 4.5 litres (3.8cm de diamètre et 4m de longueur) à une température de 460°C et sous une pression de 13.89 MPa.

Le fonctionnement de l'installation pilote a été régulier et la pression a subi un abaissement minime de moins de 0.4 MPa. A la fin des 21 jours d'opération, le séparateur à haute température, les préchauffeurs et toutes les conduites de transfert étaient exempts de résidus. Par contre, il y avait un dépôt dur et poreux couvrant une surface de 3m le long du réacteur. Bien que pendant cette marche, la consommation d'hydrogène a été supérieure à celle d'un cycle analogue contenant aucun catalyseur, le dépôt de coke était plus élevé. La raison de cette plus grande cokéfaction est que le point de fusion de la houille était bas et par conséquent une accumulation de cendre dans le liquide du réacteur a pris place.

Plus de soufre a été récupéré pendant cet essai que pendant une marche effectuée dans des conditions analogues mais sans additifs. Le surplus de gaz d'hydrogène sulfuré dans le système ne causa aucun problème.

Les droits de la Couronne réservés

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INTRODUCTION

A coal-base catalyst containing cobalt, molybdenum and alumina was used in the hydrocracking of Athabasca bitumen. The primary objective was to assess the effect of catalyst addition on solid deposition, and to compare performance with a similar run without catalyst. A secondary objective was to study the effect of a coal-base catalyst on pitch conversion, product distribution, and sulphur and nitrogen removal to be documented in a subsequent report.

Bitumen obtained from the tar sands contains about 51 wt % pitch (fraction boiling above 524°C equivalent atmospheric boiling point) which must be converted to distillable hydrocarbons, either by a coking process such as delayed or fluidized coking (1), or by a hydrogenation process such as thermal hydrocracking (2). On the basis of extended runs (3), thermal hydrocracking has proven to operate at a relatively high pressure of 24.2 MPa, and at a liquid hourly space velocity (LHSV) of 2 without reactor fouling. The present study is part of a program aimed at reducing capital cost by attempting to operate at lower pressures while minimizing coke formation. This program is based on experiments in a 4.5-L pilot-scale reactor operating in the plug-flow mode with bottom feed of liquid and gas. The development of an economical process for the refining of Canada's low grade tar-sands bitumen is one of the objectives of CANMET (Canada Centre for Mineral and Energy Technology), consistent with the policy of the Department of Energy, Mines and Resources of ensuring the effective use of Canada's mineral and energy resources.

Athabasca bitumen contains 4-5 wt % sulphur, which has to be reduced to meet existing sulphur standards. Co-Mo-alumina catalysts are satisfactory for desulphurization reactions. McColgan and Parsons observed that catalysts containing a Co/Mo ratio of 0.64 or more were most active towards desulphurization (4). Alumina promotes condensation of larger molecules on the surface of the catalyst, thereby removing potential coke precursors. The choice of coal to provide a nucleus for coke deposition over other coke carriers was made because coal is cheap and, under hydrocracking conditions, a portion of the coal hydrogenates thus increasing the distillate yield. A 74 to 250-µm high volatile bituminous coal was used in these studies in order

that the coal and catalyst coating remain in the reactor for a sufficient period of time before becoming hydrogenated, devolatilized and swept out. It was felt that higher rank coals would be too resistant towards hydrogenation and lower rank coals (lignite) would readily break up. Earlier studies have indicated that a build-up of catalyst is desirable (5).

PREVIOUS WORK

Petroleum stocks are extremely complex mixtures of compounds containing, in addition to carbon and hydrogen, significant quantities of sulphur, nitrogen, oxygen and various metals. These compounds vary in type, molecular structure, molecular weight and physical properties. When exposed to high temperatures in a hydrogen atmosphere they are subject to cracking reactions and reduction by hydrogen. According to Greensfelder et al. (6) and Appleby et al. (7), the major reaction of aromatics under cracking conditions is dehydrogenation and condensation with the ultimate formation of coke. Since polynuclear aromatics present in the bitumen do not crack readily, they contribute towards coke formation (8). According to Belinko and Denis (9), formation of coke-like deposits during thermal hydrocracking of bitumen cannot be prevented but only minimized under appropriate conditions. Coke thus formed, together with the mineral matter present in the feed, will deposit on the walls of the reactor or other equipment under any conditions, eventually causing shut-down of the unit. The coking can be reduced and reactor deposits greatly minimized at high hydrogen pressure (3). Another method of reducing the formation of reactor deposits is to add a material "getter" which provides sites for the deposition of coke precursors. The continuous addition and withdrawal of this "getter" material provides a mechanism for removal of solids from the system. The fact that coke from bitumen will deposit on coal particles has already been established (10). Furthermore, it has been shown that some of the coal is hydrogenated under conditions used to hydrocrack the bitumen (11). Preliminary bench scale studies have shown that a further diminution of reactor deposits can be achieved if a Co-Mo-alumina catalyst is present on the coal surface (12).

The mineral matter present in the feed plays an important role in coke deposition. Chervenak and Wolk (13) observed that feed containing high mineral content (> 1 wt %) had less tendency to form coke in the reactor than feed containing low mineral matter (< 1 wt %). Bench scale studies conducted by McColgan et al. (14) indicated that a higher mineral content had no apparent effect on pitch conversion and desulphurization, but suppressed coke deposition in the reactor and general reactor fouling.

Wolk (15) claimed that when the mineral concentration of the reactor fluid was maintained between 4 and 10 wt % during thermal hydrocracking, no coke was found in the reactor. It seemed that during the hydrocracking process, carbonaceous material deposited on solid particles instead of the reactor wall, and could thus be carried out with the reactor effluent. This indicated the possibility of continuously adding and withdrawing a coke carrier in the reactor. The addition of coke carriers was first proposed by Schuman (16) who suggested the use of "getters" such as sand, quartz, alumina, magnesia, zircon, beryl or bauxite. These "getters" could be regenerated after use by heating the fouled carrier with oxygen and steam at about 1090°C to yield regeneration-product-gases containing a substantial amount of hydrogen. In an attempt to reduce operating expenses due to catalyst fouling, Ternan and Parsons (11) used coal as a "coke getter" and observed that coal particles were able to accumulate metals and any coke formed during the hydrocracking process. Petrographic analysis of the fouled coal revealed that deposits of coke on the surface of the particles originated primarily from the oil residuum rather than from the coal itself (10). Belinko et al. (17) observed that coke precursors deposit on coal particles present in the bitumen.

EXPERIMENTAL

Apparatus

Experiments were carried out in a $4.5-\ell$ reactor with an inside diameter of 0.038 m. This reactor and peripheral equipment have been described in detail in an earlier report (5).

Catalyst

The catalyst was made using $Co(NO_3)_2.6H_2O$ and $(NH_4)_6MO_7O_{24}.4H_2O$ powders dissolved in water and then mixed with $Al_2O_3.H_2O$ gel. The resulting gel was then mixed with coal to give a catalyst with 15% by weight of metal oxides and 85% coal. For 42.5 kg of coal the following amounts of chemicals were added:

$Co(NO_3)_2.6H_2O$	1.65 kg
(NH ₄) ₆ Mo ₇ 0 ₂₄ .4H ₂ 0	1.10 kg
A1203.H20	7.23 kg
H ₂ O	16.0 kg
HNO	0.14 kg

The mixture was stirred until homogeneous, and the water was evaporated at approximately 100°C in a stream of dry air. The coal-based catalyst was screened through a 30-mesh (Canadian Standard) sieve to remove larger part-icles before use.

To obtain a homogeneous mixture, a weighed amount of coal-base catalyst (550 g) was mixed manually with approximately 3 kg bitumen at 60° C. This mixture was then poured into a feed tank containing about 20 kg of bitumen with the feed-tank mixer operating. Finally the feed-tank was filled to 27 kg with bitumen. The feed-tank mixer with a 3-bladed 4-in. dia propeller was kept at 200 rpm about 3 in. up from the tank bottom and the tank was main-tained at 100 to 110° C under 14 kPa nitrogen pressure until the feed was used.

Start-up Procedure

The reactor and hot separator were heated to 350° C with hydrogen circulating at 0.0527 Std m³/h. Feed with no catalyst was then introduced at a flow rate of 9000 g/h, and the reactor was heated to 430° C. The temperature of the reactor was maintained at 430° C for one hour, and then raised 5° C every hour until 460°C was reached. Feed containing the coal-base catalyst was then introduced at the required flow rate (9000 g/h).

To assess the effect of catalyst on coking in the reactor and to determine the changes in coal as it moved along the length of the reactor, reactor liquid samples were withdrawn from three levels of the reactor - bottom, middle and top - into a Kuentzel bomb (KB). Experimental details regarding KB and reactor-liquid sample-withdrawal procedure are described in a previous paper (17).

RESULTS AND DISCUSSION

Identification numbers, pilot plant run numbers and reaction conditions for the three runs compared in this report are given in Table 1. Run CBC460 represents the run with the Co-Mo-alumina catalyst coated on high volatile A coal. The analysis of this run has been made for the start-up period, steady state, a one-day catalyst-withhold period and the end of run. The shaded portion in all figures represents the catalyst-withhold period. Runs RS460 and NRS460 represent two extended runs without any additive or catalyst. These runs were carried out previously and were briefly described in another report (3). In run RS460 there was extensive liquid sampling from the bottom of the reactor (RS = Reactor sampling). In run NRS460, no reactor liquid samples were taken from the reactor.

Two different liquid products were taken from the plant - the heavy ends (HE) which contained all of the pitch and some distillate, and the light ends (LE) which contained no pitch and the balance of the distillate. This separation of distillate material, LE and HE, depended on the hot separator temperature and the gas/liquid ratio in the separator. Properties of LE and HE which are important to plant operation are discussed in this paper. Properties of the distillate and pitch will be presented in a subsequent report.

Plant Operation

As soon as feed containing the catalyst was introduced into the system, problems were encountered in pumping, especially when switching the feed from one tank to another. The exit line from the feed tank plugged and the feed could not be pumped for periods up to 8 min. This problem was observed throughout the entire run. It was also observed that when the catalyst was mixed with bitumen, some small lumps were formed which were removed by a coarse screen when the mixture was poured into the feed tank. To avoid such pumping problems, a better method for mixing the catalyst or coal with the bitumen should be developed. During the course of the run the skin temperature at the top of the reactor had to be raised from 450° C to 490° C to maintain a temperature of 460° C inside the reactor. This indicated coke and mineral matter deposition on the wall. After the run, when the plant was inspected, the reactor was found to contain carbonaceous deposits in the top 3 m, details of which are given in the latter section of this report.

Feed and product flow rates were fairly constant during the run except for the heavy ends which increased in the latter stages (Fig. 1). This resulted from a decrease in pitch conversion (18) or a decrease in hydrocarbon gas make (Fig. 2).

Figure 3 shows the variation in total system-pressure drop for all three runs. For CBC460, the pressure drop varied between 0.1 and 0.4 MPa. For RS460 and NRS460, on the first day only, it increased to 0.5 MPa and during operation it increased to over 1.0 MPa. A low constant pressure drop is desirable as it is an indication that lines are clear of deposits.

Reactor Fluid

There were problems in obtaining reactor fluid samples. The Kuentzel bomb or the lines between it and reactor were totally plugged on some occasions. Hence samples from all three points of the reactor could not be taken during the entire run. Analyses of samples collected are given in Table 2.

On the fourth day, the ash content of the fluid at the bottom of the reactor was 41.95 wt %. At the middle and top of the reactor, the ash content of the reactor fluid was 14.35 and 4.32 wt %, respectively. The cobalt-to-molybdenum ratio in the ash was nearly the same at all points (0.275 ± 0.015) which indicated that the catalyst was equally distributed throughout the reactor. These data also revealed that the main constituent of the ash was the catalyst.

Samples taken on the eleventh day of the run contained 67.7 wt % ash content in the reactor fluid. It was recognized that this was too high in a commercial reactor and that the ash content would have to be controlled at a lower level, below about 30 wt %. The catalyst was withheld from the

feed for one day to see the effect this would have on the system. Unfortunately, no further samples could be withdrawn from the bottom of the reactor, but it was clear that withholding approximately 3600 g of coal-base catalyst over 24 hours had an effect as shown by the decrease in ash content in samples from the middle of the reactor.

As an analysis of reactor fluid could not be obtained for the entire run, it was difficult to relate the reactor fluid properties to coke deposition on reactor walls. On the seventh day of the run, asphaltenes and BIOR (benzene insoluble organic residue), which are supposedly responsible for coking, were 9.2 and 12.8 wt %, respectively at the reactor bottom. At the middle of the reactor, the amount of BIOR was 20.8 wt %. Such a high value may have been the result of product liquid evaporation. At the top of the reactor it was 6.6 wt % which is inconsistent with the above, and awaits further explanation, perhaps in terms of hydrogenation of the coal which would reduce benzene-insolubles. Microscopic analyses (19) indicated that coal was being hydrogenated as it moved up in the reactor. Some of the coal converted to coke with "bitumen coke" depositing on it.

Inspection Samples

After shutdown, samples were collected from inside the reactor and from other parts of the plant. Table 3 shows the analyses of these samples. The sample from the top of the reactor contained 31.65 wt % ash whereas the sample from the bottom of the reactor contained 57.10 wt % ash. It had been observed previously (3) that coking starts from the top of the reactor and grows inward and downward to the lower portion. These analyses are consistent with that theory, with the early coke deposit acting as a trapper filter resulting in higher ash levels in the lower portion of the reactor. Sulphur content in inspection samples from the gas traps was about 20 wt %, suggesting high sulphur removal in this experiment compared with non-catalytic runs.

Inspection After Completion of Run

After completion of the run, when the reactor was opened for inspection, deposits of coke and mineral matter were detected between about 23 cm from the top to about 78 cm from the bottom. There was an irregular hole of about 0.3 cm dia in the middle, extending along the length of the reactor

through which all the liquid and gases were passing. The bottom of the reactor had a ring of solids about 0.6 cm thick. The material was hard and porous and mechanical cleaning was not possible. To estimate the volume of the deposit and its porosity, varsol was pumped into the reactor. The total amount of varsol added to fill the reactor was 3140 ml of a possible 4500 ml (reactor volume), giving a volume of solids of $V_s = 1360$ ml and a porosity ε for the deposit of 0.6 ($\varepsilon = (V_D - V_S)/V_D$ where V_D was the volume of the reactor occupied by the deposit). This indicated that the deposit was extremely porous and had numerous interstitial spaces.

The transfer line between the reactor and the hot separator, the emergency line and preheaters were free of any deposits. Gas lines in the system were coated with a black oil, and the light ends receiver and water scrubber contained some heavy oil indicative of reverse flow in the system.

Traps located upstream of the gas recycle pump had white crystal deposits and the downstream trap had white crystals and oil-like deposits as well. These materials contained about 20 wt % sulphur (Table 3).

Light Ends (LE)

Figure 4 shows the variation in the LE properties during the run. The specific gravity $(60/60^{\circ}F)$ increased slightly with the run time. The sulphur content decreased initially to a steady state value of about 0.46 wt %, then increased dramatically during the period when the catalyst was withheld and decreased again to a steady state value when the catalyst was re-introduced. This is a strong indication that the catalyst was in dynamic balance, with fresh catalyst make-up being as important as catalyst hold-up. As the catalyst built up in the reactor, sulphur removal increased and sulphur content in LE decreased. The nitrogen content initially decreased and then became nearly constant. It seems that the catalyst had only a slight effect on nitrogen removal.

Heavy Ends

Figure 5 shows the variation in the properties of HE. In the latter stages of the run, the specific gravity and ash content increased slightly. Initial decrease in the sulphur content was probably due to catalyst build-up in the reactor. Sulphur content was nearly constant over

the steady-state period, and increased slightly in the catalyst-withhold period. Nitrogen content decreased slightly. The concentration of asphaltenes(difference between pentane- and benzene-insolubles) was nearly constant but that of BIOR increased to a maximum and then decreased, with no apparent correlation with catalyst addition. A study to elucidate the relationship between BIOR formation and pitch conversion would help to explain the decreased amount of coke in HE of this run.

GENERAL DISCUSSION

Compared with runs RS460 and NRS460, the operation of the pilot plant for CBC460 was smooth. The flow rates and temperatures at all points were steady, except for skin temperature at the reactor top which was raised to 490° C to maintain temperature inside the top of the reactor at 460° C. The total system pressure drop was steady and was much lower than in run RS460 and NRS460. Solid deposition in the reactor was much higher for CBC460. For RS460 deposits built up in the top quarter of the reactor only, whereas for CBC460 the reactor was nearly full. Analyses of inspection samples indicated that coke formation started from the top.

It has generally been found that coke formation is a major determining factor on the operability and life of the process. It has also been established that the presence of asphaltenes and condensed polycyclic aromatics (coke precursors) in the reactor fluid favour the formation of coke deposits in the reactor. This run was conducted with the hope that coke precursors would precipitate on coal particles and be removed with reactor effluents and thus avoid reactor fouling. However, the reactor was found to be full of coke and other carbonaceous deposits.

The coal used in the present study was a high volatile coal (VM = 32.4 wt %). As the coal entered the reactor bottom, it apparently started melting and hydrogenating, thereby releasing volatile matter. It moved along the length of the reactor, leaving behind some catalyst and mineral matter which settled in the reactor causing the concentration of ash to increase to 67.7 wt \% for run CBC460 compared with a maximum of 21 wt \% for RS460. There is evidence to suggest that asphaltenes and coke pre-

cursors precipitate on solid particles (16,17). It seems that mineral matter may have provided nuclei for coke deposition. As these particles moved upward they grew in size and, because of product liquid evaporation, their concentration increased to the extent they started depositing on the walls of the reactor together with mineral matter, ultimately plugging the reactor.

It is possible that the coal particles were too large as the mesh size -60 +200 Canadian Sieve contained some much larger than those found in the bitumen after centrifuging; i.e., 5-50 μ m, (3). However, simple calculations show that a large proportion of coal must have disappeared as 65% ash material corresponds to a large amount of coal.

From the present investigation it seems that this coal is not suitable for removing coke precursors and that a high ash content in the reactor fluid may not be desirable. Keeping these observations in mind for future runs, a coal with a higher softening point should be selected.

Table 4 shows the properties of LE and HE for all three runs. Specific gravity and sulphur content in LE and HE decreased for run CBC460. Even in the catalyst-withhold period, sulphur content in LE and HE was much less than for RS460 and NRS460, probably because of catalyst build up in the reactor. From Fig. 4 and 5 it is clear and the sulphur content increased in the catalyst-withhold period, supporting this argument. Even with high sulphur removal there were no problems of line plugging due to metal or ammonium sulphide deposition.

SUMMARY AND CONCLUSIONS

- The pilot plant operation was smooth and there were no major problems except for pumping the feed when switching from one tank to another, probably caused by catalyst mixing procedure. A better method should be developed for mixing catalyst to avoid this.
- 2. The total system pressure drop was less than 0.4 MPa over the entire run whereas it was more than 0.5 MPa for the runs without any additive.
- 3. Hot separator, preheaters and transfer lines were clean except for some carry-over due to back flow.

- 4. The reactor was full of deposits probably because of the large particle size and properties of the coal. For reducing reactor fouling, a coal with a high softening point should be used.
- 5. The catalyst had little effect on BIOR and asphaltenes content in HE.
- 6. The sulphur content was about 0.5 wt % in LE and about 2.2 wt % in HE compared with 1.3 and 3.3 wt %, respectively for the runs without any additive.
- 7. The product specific gravities 60/60⁰F were lower for the run with a catalyst.
- 8. There were no problems in handling the extra hydrogen sulphide in the system resulting from higher removal.
- 9. The catalyst was in dynamic balance indicating that fresh catalyst makeup was as important as catalyst hold-up in the reactor.

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REFERENCES

- Gray, G.R. "Conversion of Athabasca bitumen"; AIChE Symposium Series;
 v. 69, no. 127, pp 99-102; 1973.
- 2. Merrill, W.H., Logie, R.B. and Denis, J.M. "A pilot scale investigation of thermal hydrocracking of Athabasca bitumen"; Mines Branch Research Report R-281; Dec. 1973.
- 3. Pruden, B.B., Logie, R.B. and Denis, J.M. "Thermal hydrocracking of Athabasca bitumen: Reduction of reactor fouling"; CANMET (Canada Centre for Mineral and Energy Technology, formerly Mines Branch), Department of Energy, Mines and Resources, Report 76-33; Aug. 1976.
- 4. McColgan, E.C. and Parsons, B.I. "The hydrocracking of residual oils and tars". Part 2; Mines Branch Research Report R-253; Aug. 1972.
- 5. Khulbe, C.P., Pruden, B.B., Denis, J.M. and Merrill, W.H. "Pilot plant thermal hydrocracking of GCOS (Great Canadian Oil Sands) bitumen; 1 effect of heavy-oil recycle on pilot plant operation"; CANMET Report 76-28; June 1976.
- 6. Greensfelder, B.S., Vogue, H.H. and Good, G.M.; Ind. Eng. Chem; v. 5, no. 3, p 19; 1957.
- 7. Appleby, W.G., Gibson, J.W. and Good, G.M.; Am. Chem. Soc., Div. Petrol. Chem.; v. 5, no. 4, p 71; 1960.
- 8. Gully, A.J. and Ballard, W.P. "Hydrogenation of catalytic cracking charge stocks"; Adv. Pet. Chem. Ref.; v. 7, p 241; 1963.
- 9. Belinko, K. and Denis, J.M. "Some chemical aspects relating to the formation of coke during thermal hydrocracking of bitumen"; CANMET Laboratory Report ERP/ERL 76-181 (R); Sept. 1976.
- Nandi, B.N., Ternan, M., Parsons, B.I. and Montgomery, D.S. "Coke formation during simultaneous hydrocracking of bitumen and hydrogenation of coal"; Fuel; v. 54, p 147; July 1975.
- 11. Ternan, M. and Parsons, B.I. "Hydrocracking Athabasca bitumen in the presence of coal", Part 2; CANMET Scientific Bulletin CM 75-10; May 1975.
- 12. Ternan, M. unpublished work.
- 13. Chervenak, M.C. and Wolk, R.H. "Treating tar sands"; U.S. Patent 3,775,296; Nov. 27, 1973.
- McColgan, E.C., Soutar, P.S. and Parsons, B.I. "The hydrocracking of residual oils and tars", Part 3; Mines Branch Research Report R-256; 1972.

- 15. Wolk, R.H. "Hydroconversion of tar sand bitumen"; U.S. Patent 3,244,937; Oct. 29, 1974.
- 16. Schuman, S.C. "Heavy oil conversion with low coke formation"; U.S. Patent 2,875,150; Feb. 24, 1959.
- 17. Belinko, K., Nandi, B.N. and Denis, J.M. "The distribution of coke precursors in the reactor during thermal hydrocracking of Athabasca bitumen"; CANMET Laboratory Report ERP/ERL 76-186 (J); Nov. 1976.
- Khulbe, C.P., Pruden, B.B. and Denis, J.M. "Thermal hydrocracking of Athabasca bitumen, 2: Effect of coal-base catalyst on product quality"; CANMET Laboratory Report ERP/ERL 77-12 (R).
- 19. Nandi, B.N., Pruden, B.B. and Parsons, B.I. "Microscopic changes in the coal for coal-base catalyst used in the hydrocracking of Athabasca bitumen"; CANMET Laboratory Report ERP/ERL 76-177 (J).

Run No.	Pilot Plant Run No.	Duration	Recycle Gas Flow	Hydrogen Gas Purity	LHSV (Nominal)	Feed Flow (Average)	Reactor Temp	Pressure	Reactor Volume	Catalyst
		h	m ³ /h	% Н ₂		g/h	°C	MPa	L	
CBC460	87-1-1	452	0.052	85	2	8583	460	13.89	4.5	Co-Mo- Alumina on coal
RS460	71-1-2	480	0.052	. 85	2	7972	460	13.89	4.0	Nil
NRS460	71-1-3	308	0.052	85	2	7936	460	13.89	4.0	Nil

TA	BL	E	1

Identification Numbers and Reaction Conditions for Different Runs

TABLE 2

Properties of the Reactor Fluid, Run CBC460

Sample Point of Reactor	Day	PI* wt %	BI* wt %	Asphal- tene wt %	Ash wt %	BIOR* wt %	CCR* wt %	S wt %	V ** wt %	Ni ** wt %	Co wt %	Mo wt %
Bottom	4	-	-	_	41.95	_	-	-	-	-	2.52	9.83
	7	48.8	39.6	9.2	26.80	12.8	57.4	6.06	1.8	0.53	-	-
	11 (A)	-	-	-	67.70	-	94.5	11.52	6.0	1.7	-	-
	11 (B)	72.3	61.7	10.6	51.00	10.7	71.7	9.02	4.8	1.4	-	-
Middle	4	-	-	-	14.35	_	-	-		_	2.17	7.51
	7	64.7	57.9	6.8	37.1	20.8	66.4	6.20	2.9	0.83	-	-
	11	71.1	62.4	8.7	38.5	29.3	59.1	6.63	3.1	0.95	-	-
	14	-	-	-	7.97	-	-	-	-	-	-	-
	18	50.5	47.4	3.1	20.6	26.8	69.5	-	-	-	-	-
Тор	4	-	-	-	4.32	_	-	-	_	-	-	_
	7	24.6	11.4	13.2	4.80	6.6	27.1	2.54	803 ppm	203 ppm	_	-

* PI - pentene-insolubles, BI - benzene-insolubles, CCR - Conradson carbon residue, BIOR - Benzene insoluble ** wt % except ppm where noted organic residue

TABLE 3

Analyses of Inspection Samples, Run CBC460

Inspection Samples	Ash wt %	Sulphur wt %
Top of reactor	31.65	-
Bottom of reactor	57.10	-
30" from bottom of reactor	57.22	· _
Trap after the gas pump:		
Тор	-	20.98
Bottom	_ ·	22.77
Trap before gas pump:		
Тор	-	18.87
Bottom	-	20.38

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TABLE 4

Run N	0.		CI	RS460	NRS460		
		Start-up	Steady State	"Catalyst withheld'	End	Ave.	Ave.
				LE	•		
Sp gr Sulphur	60/60 ⁰ F wt %	0.808 0.55	0.817 0.45	0.815 1.66	0.799 1.32		
Nitrogen ppm		913	818	671	770	-	563
			u 				
Sp gr	60/60 ⁰ F	0.954	0.968	0.976	0.974	0.991	0.976
Sulphur	wt %	2.12	1.64	2.28	1.89	3.45	3.30
Nitrogen	wt %	0.46	0.40	0.41	0.39	-	0.51

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Shaded portion represents a period without catalyst addition.







Shaded portion represents a period without catalyst addition.



FIGURE 5 - Variation in HE Properties for Run CBC460 Shaded portion represents a period without catalyst addition.

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