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EVALUATION OF A TWO-STAGE THERMAL AND CATALYTIC HYDROCRACKING PROCESS FOR ATHABASCA BITUMEN

R. Ranganathan, B.B. Pruden, M. Ternan and J.M. Denis

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EVALUATION OF A TWO-STAGE THERMAL AND CATALYTIC HYDROCRACKING PROCESS FOR ATHABASCA BITUMEN

bу

R. Ranganathan*, B.B. Pruden**, M. Ternan** and J.M. Denis***

ABSTRACT

A two-stage thermal and catalytic hydrocracking process of upgrading Athabasca bitumen is described. In the first stage, the bitumen is treated in the presence of excess hydrogen in a tubular reactor at 13.90 MPa and 450° C. A heavy-oil product is separated and a portion is recycled to the reactor. The light-oil product in vapour form is further treated in a vapour-phase catalytic reactor to remove sulphur and nitrogen compounds.

The second stage of this process is simulated by treating the light oil once-through in a bench-scale fixed-bed catalytic reactor. The results for catalytic treatment at 13.90 MPa and 430°C suggest that the specifications of reformer naphtha feedstock, fuel oils and cat-cracking gas-oil feedstock can be met. Three different catalysts, namely, Co-Mo on alumina, Ni-Mo on alumina and Ni-W on alumina, are evaluated in the catalytic hydrocracking stage and their selectivities are compared.

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^{*} Project Leader, ** Section Heads and *** Manager, Synthetic Fuel Research Laboratory, Energy Research Laboratories, Canada Centre for Mineral and Energy Technology, Dept. of Energy, Mines and Resources, Ottawa, Canada.

L'EVALUATION D'UN PROCEDE D'HYDROCRAQUAGE THERMIQUE ET CATALYTIQUE À DEUX PHASES EMPLOYE POUR TRAITER LE BITUME DE L'ATHABASCA

par

R. Ranganathan*, B.B. Pruden**, M. Ternan** et J.M. Denis***

SOMMAIRE

Dans ce rapport, les auteurs décrivent un procédé d'hydrocraquage thermique et catalytique à deux phases qui est employé pour améliorer du bitume de l'Athabasca. Pendant la première phase, le bitume est traité en présence d'un excès d'hydrogène dans un réacteur en forme de tube sous une pression de 13.90 MPa et à une température de 450° C. Un produit d'huile lourde est séparé du bitume et une portion est recyclée dans le réacteur. Puis, la vapeur d'huile légère est traitée à nouveau dans un réacteur catalytique à phase vapeur afin d'en retirer les composants de soufre et de nitrogène.

La deuxième phase de ce procédé est simulée en laboratoire, par le traitement de l'huile légère, hydrocraquée une seule fois, dans un réacteur catalytique à lit fixe. Les résultats de ce traitement, effectué sous une pression de 13.90 MPa et à une température de 430°C, suggèrent que les spécifications d'une charge d'alimentation de réformation en naphta, des huiles lourdes et de la charge d'alimentation en gaz-huile du craquage catalytique peuvent être atteintes. Les auteurs font l'évaluation de trois catalyseurs différents, à savoir Co-Mo/alumine, Ni-Mo/alumine et Ni-W/alumine, pendant la phase de l'hydrocraquage catalytique et ils comparent leurs caractères sélectifs.

Droits de la Couronne réservés

^{*} Chef de projet, ** Chefs de section et *** Gestionnaire, Laboratoire de recherche sur les combustibles synthétiques, Laboratoires de recherche sur l'énergie, Centre canadien de la technologie des minéraux et de l'énergie, Ministère de l'Energie, des Mines et des Ressources, Ottawa, Canada.

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INTRODUCTION

The thermal hydrocracking process has been found, on the basis of pilot-plant-scale runs (1,2), to give a high distillate yield and to eliminate the production of waste coke in the processing of Athabasca bitumen. This work was undertaken to further develop the thermal hydrocracking process, in keeping with the Energy Research Program of the Canada Centre for Mineral and Energy Technology, Department of Energy, Mines and Resources, and its policy of ensuring the effective use of Canada's mineral and energy resources.

The distillate from the thermal hydrocracking reactor contains high amounts of sulphur and nitrogen. Following the hydrocracking step, the product is distilled to produce naphtha at IBP-204°C, light gas-oil at 204-343°C and heavy gas-oil at 343-524°C, and these are further treated individually to remove sulphur and nitrogen compounds. Industry, by tradition, has always treated the product in individual fractions and because of fears that nitrogen compounds would migrate to the naphtha fraction, producing off-specification material. Once-through treatment of the combined distillates has advantages in the reduction of capital and operating costs for distillation facilities and hydrotreaters. Further reduction in costs can be obtained if the hot hydrocracked product from the first stage is treated directly without pressure let-down or condensation. It is the objective of this work to investigate the once-through hydrotreatment of combined distillate to prove the two-stage thermal and catalytic hydrocracking process (CDH process).

In the proposed CDH process, liquid feed and hydrogen would enter a thermal hydrocracking reactor and a large portion of the pitch boiling above 524°C would be converted to distillate material. The reactor products would then be treated to separate the residual pitch from the distillate. This pitch, containing most of the troublesome materials, would be withdrawn for gasification or sale as a by-product. The distillate, hydrocarbon gases and hydrogen at high temperature and pressure would enter a second-stage catalytic reactor for desulphurization and denitrogenation.

LITERATURE SURVEY

A two-stage catalytic hydrocracking process was tested by Quinsey et al. (3) for upgrading vacuum residuum from Weyburn crude. They used slurry-type catalytic hydrocracking in the first stage and a down-flow fixedbed hydrocracking in the second stage. Several reports have been published on two-stage catalytic hydrocracking of heavy oils (4,5). However, only a few authors (6,7,8) have attempted to use non-catalytic hydrocracking in the first stage. Gatsis (6) described a non-catalytic first stage where 2-30 wt % water and hydrogen were contacted counter-currently with heavy oil in a tubular reactor packed with stainless steel turnings. Schlinger et al. (7) and Brodeur and Schlinger (8) used a non-catalytic first stage where the heavy oil and hot hydrogen were contacted counter-currently. The heavy oil was fed in at the top of the contacting tower. In the above patents no mention was made of meeting the distillate feedstock and fuel oil specifications by using a two-stage upgrading process. In all cases, the heavy oil from the bottom of the first-stage contacting tower was recycled to either the top or to the mid-section of the tower.

In second-stage upgrading, the distillate oil stream is conventionally divided into naphtha at IBP-204°C, light gas-oil at 204-343°C and heavy gas-oil at 343-524°C before hydrotreating. A few studies have been reported on treating the fractions in a single stream, and the reported results indicate that this would transfer more nitrogen compounds from high-boiling into low-boiling fractions. Frost and Poulson (9), using a down-flow hydrotreating system, showed that even though the total nitrogen content of the product from one-step hydrotreating compares with that from a multi-step process, the nitrogen is present in significantly higher concentrations in the naphtha and light gas-oil fractions. This poses a problem since the reformer naphtha feedstocks should contain less than 1 ppm nitrogen. In the case of sulphur removal, Frost and Poulson (9) did not observe any such difference between the single-step and multi-step processes. Further, they found greater yields of naphtha and light-oil fractions in the single-step process.

EXPERIMENT

The properties of Athabasca bitumen are listed in Table 1. Of interest are the high sulphur, nitrogen and ash contents compared with conventional crude. The bitumen contains 51.5% of material boiling above 524°C, 4.48 wt % sulphur and 0.5 wt % nitrogen. The schematic of the proposed twostage thermal and catalytic hydrocracking process (CDH) is shown in Fig. 1. The bitumen and hydrogen are mixed and flow up through a tubular reactor. The temperature is maintained at 450° C and the pressure at 13.9 MPa. mixture of gas and liquid from the top of the tubular reactor enters the hot separator which is kept at the same temperature as the reactor. Liquid from the hot separator is recycled to the tubular reactor, with a portion continuously withdrawn to prevent accumulation of metals and mineral matter. The gases from the hot separator are sent to an up-flow fixed-bed catalytic hydrocracker which is the second stage of the CDH process. The pressure in the catalytic reactor is the same as in the tubular reactor but the temperature is selected to meet the product specifications. The details of typical reaction conditions in the first- and second-stage reactors are given in Table 2.

In the work discussed here, the second-stage catalytic hydrocracking was simulated using a bench-scale reactor unit previously described in detail (10,11,12). The reactor was sequentially filled from the bottom with 42 ml of berl saddles, 100 ml of catalyst pellets and 13 ml of berl saddles. In a typical run, feed and hydrogen flowed up through the fixed catalyst bed. Gas and liquid reaction products were separated downstream. After steady-state conditions had prevailed for one hour, liquid product was collected for two hours. The hydrogen used was 99% pure but, in an actual CDH process, recycle gas would contain some hydrogen sulphide and hydrocarbon gases. However, this would not affect the results as the recycle gas purity is reported to have no effect on the product quality (13).

Previous studies (12) have shown that catalytic pre-treatment is important in obtaining stable catalytic activity. Pre-treatment was carried out with feedstock at reaction conditions of 13.9 MPa, 400° C, liquid hourly space velocity of 2.0 and 883 m³API/t hydrogen for two hours.

The reaction studies were carried out at various temperatures.

The stability of the catalyst was checked at the end of a series by repeating the first experiment in the series.

Feed for this bench-scale unit was obtained from the thermal hydrocracking experiment described previously (14). It consisted of the light ends from pilot-plant run R-2-1-2 with properties as in Table 4. This light-ends stream contained about 86% of the total distillate product resulting from fractionation in the hot separator which had only one stage of separation. The recycle-oil purge stream contained the remainder. The recycle-oil purge stream in an operating plant would normally be distilled to yield the remainder of the distillate, which would be fed to the inlet of the second-stage catalytic hydrocracker. Three commercial catalysts, i.e., 3 wt % CoO - 15 wt % MoO₃ on alumina (Harshaw Chemical Co. HT-400E), 3.8 wt % NiO - 15 wt % MoO₃ on alumina (American Cynamide Co. Aero HDS-3A) and 6 wt % Ni - 19 wt % W on alumina (Harshaw Chemical Co. 4301E), were evaluated in the bench-scale unit. These catalysts were chosen because of their wide use in commercial hydrotreating.

It should be noted that sulphur and nitrogen balances could not be obtained between total liquid and its distilled fractions for the data presented in Tables 4, 5, 6 and 7. This might be caused by the removal of dissolved gases during distillation. To avoid this problem, nitrogen is usually bubbled through the samples before analysis. This could not be done for the samples obtained in this work because the naphtha might be selectively removed. However, the comparisons and conclusions should not be affected as they are based on the results of distilled fractions.

RESULTS AND DISCUSSION

Thermal and Catalytic Hydrocracking

Typical results for the total product from the first-stage thermal hydrocracking are given in Table 3. Pitch conversion of 81.5% and sulphur removal of 52.2% were obtained and only 17.8% nitrogen was removed. The feed from the first stage to the catalytic hydrocracker would have properties as in Table 4. In this table, the total feed is reported in terms of its overall properties and the properties of its constituent naphtha, light gas-

oil and heavy gas-oil fractions. Even though some of the troublesome constituents were hydrocracked into less refractory constituents during thermal hydrocracking, the distillates still contained unacceptable amounts of sulphur and nitrogen compared with conventional crude oil distillates.

Results for catalytic hydrocracking at a liquid hourly space velocity of 1.0, 13.9 MPa and at several temperatures, with a 3.0 wt % CoO -12 wt % MoO₂ on alumina catalyst, are shown in Table 5. It is seen that, except for the sulphur contents, the 400°C experiment showed reproducible results at the beginning and completion of the series. This shows that the catalyst was not deactivated during the experimental sequence lasting 12 The volumetric and weight yields were higher than 91.3% and 86.4% respectively. Compared with the composition of the feed to the catalytic hydrocracking unit, the naphtha and light gas-oil contents increased considerably. The heavy gas-oil content decreased from 21.3 vol % to as low as 5.9 vol %. The specifications for reformer naphtha feedstocks, fuel oils and catalytic cracking gas-oil are also listed in Table 5. It is seen that the fractions obtained from the hydrocracked product easily met all the specifications except for the sulphur content in the naphtha fraction. The nitrogen content data did not show any transfer of nitrogen compounds from higherboiling fractions. Frost and Poulson (9) reported that, in once-through hydrocracking of shale oil on a Ni-Mo catalyst, the IBP-177°C fraction contained about 83 ppm nitrogen compared with 5 ppm nitrogen in the 177-288°C fraction. On the contrary, the results with Co-Mo on alumina catalyst in this work showed that naphtha contained less nitrogen than the light gas-oil fraction. The differences, discussed in the next section, could be due to differences in the catalysts.

In the once-through studies reported in the literature, a down-flow reactor scheme was used for catalytic hydrocracking (9) in contrast to an up-flow reactor scheme used in this study. It has been reported in the literature that an up-flow reactor scheme is superior to the usual trickle bed operation for residual feedstocks (18,19). Desulphurization, denitrogenation and demetallization conversions were better in an up-flow reactor. Montagna and Shah (19) conducted experiments for up to 100 hours and showed that for shallow beds the up-flow reactors gave better conversions than down-flow reactors and that the results were not time-dependent. Specchia et al. (20)

reported that their results indicated greater interfacial area and liquid mass transfer coefficients in an up-flow reactor compared with downward flow. Hence, it is possible that the specifications were easily met in this work because an up-flow catalytic hydrocracking reactor was used. It should be noted that at 450° C reaction temperature and liquid hourly space velocity of 1.0, the feed would be completely vaporized and the reactor would be operating as a vapour-phase reactor. At this temperature, both up-flow and downflow reactors should give similar results. However, for lower temperatures, some of the feed would be in a liquid phase and hence, because of variations in liquid hold-up and back mixing, the up-flow reactor system would give better results.

Comparison of Various Catalysts

Three different catalysts were evaluated at less severe hydrocracking conditions (LHSV = 2.0) to compare the relative activities and selectivities. The experiments were conducted at a liquid hourly space velocity of 2.0, 13.9 MPa, 883 m^3 API/t hydrogen and at different temperatures. The three catalysts studied were 3 wt % CoO - 15 wt % MoO $_{
m q}$ on alumina, 3.8 wt % ${\rm NiO}$ - 15 wt % ${\rm MoO}_3$ on alumina and 6 wt % ${\rm Ni}$ - 19 wt % W on alumina. Typical results at 460° C are shown in Table 6. The results show that the three catalysts are equally active in nitrogen and sulphur removal at this temperature. However, naphtha fractions for the products obtained from Ni-Mo and Ni-W catalysts contained more nitrogen than the light gas-oil fractions. is interesting to note that Frost and Poulson (9) had also used a Ni-Mo catalyst in the hydrocracking experiments where they observed higher amounts of nitrogen compounds in the naphtha fractions. It appears then that the phenomenon of transfer of nitrogen compounds to lower-boiling fractions depends on the type of catalyst used. This might be associated with the selectivity of Ni-Mo and Ni-W catalysts for hydrocracking. The Ni-Mo and Ni-W catalysts appeared to be more selective in hydrocracking as the yields of naphtha fraction were higher than that for the Co-Mo catalyst. Especially with the Ni-W catalyst, the naphtha fraction was extremely high. However, it is seen from Table 7 that at 400°C reaction temperature, the difference in hydrocracking selectivity was not observed. On the other hand, at this temperature, the denitrogenation and desulphurization activities were higher for Ni-Mo and

Ni-W catalysts. The results at different reaction times (Table 7) show that the denitrogenation activity dropped much faster with the Ni-W catalyst than with the other two catalysts. The nitrogen contents for the products from Ni-W and Co-Mo experiments were similar after 12 hours of reaction time. Surprisingly, the desulphurization and hydrocracking activities were not significantly affected by time on-stream. However, the effect on these activities would be noticeable if longer life studies were carried out. It should be noted that the variations in selectivities could be due in part to different methods of preparation, because these catalysts were obtained from different manufacturers.

Several reports in the literature (15,21,22) also suggest differences in selectivities of Ni-Mo, Co-Mo and Ni-W catalysts. Thomas (15) reported that Ni-Mo is superior to Co-Mo in denitrogenation. Silver et al. (21) found that Ni-W catalyst is more selective in converting quinoline-type nitrogen compounds than is the Co-Mo catalyst. However, the reported catalyst selectivities are not based on life studies. It is possible, because of poisoning, that the catalysts might not sustain the high initial activities and selectivities for a long period.

CONCLUSIONS

Results showed that the two-stage thermal and catalytic hydrocracking process could be used for upgrading Athabasca bitumen and for producing reformer naphtha feedstock, fuel oils and catalytic cracking gas-oil feedstock. Product weight yields ranging from 86.4 to 93.0% were obtained. A 3 wt % CoO - 15 wt % MoO $_3$ on alumina catalyst was found to be sufficiently active to produce specification distillates. Comparison of various catalysts showed some differences in selectivities. However, extended life studies should be carried out to substantiate the differences.

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REFERENCES

- 1. Merrill, W.H., Logie, R.B. and Denis, J.M. "Pilot scale investigation of thermal hydrocracking of Athabasca bitumen"; Mines Branch Research Report R-281; 26 p; Dec. 1973.
- 2. Pruden, B.B., Logie, R.B., Denis, J.M. and Merrill, W.H. "Thermal hydrocracking of Athabasca bitumen reduction of reactor fouling"; CANMET REPORT 76-33; 33 p; Aug. 1976.
- 3. Quinsey, D.H., Merrill, W.H., Herrmann, W.A.O. and Pleet, M.P. "Combined liquid- and vapour-phase hydrocracking of heavy oil"; Can. J. Chem. Eng.; v. 47, no. 4, pp 418-421; Aug. 1969.
- 4. Richardson, F.W. "Oil from coal"; Noyes Data Corp., New Jersey; p 268; 1975.
- 5. Johnson, A.R., Alpert, S.B. and Lehman, L.M. "Refinery applications of the H-oil process"; Proc. Div. Ref. Amer. Petrol. Inst.; v. 48, pp 815-840; 1968.
- 6. Gatsis, J.G. "Multiple-stage hydrofining of petroleum crude oil"; U.S. patent 3,453,206; July 1969.
- 7. Schlinger, W.G., Brodeur, C.H. and Marion, C.P. "Hydroconversion of hydrocarbons with the use of a tubular reactor in the presence of hydrogen and the recycling of a portion of the tar-like viscous residue"; U.S. patent 3,224,959; Dec. 1965.
- 8. Brodeur, C.H. and Schlinger, W.G. "Treatment of hydrocarbons in plural stages to produce lower boiling hydrocarbons"; U.S. patent 3,354,075; Nov. 1967.
- 9. Frost, C.M. and Poulson, R.E. "Nitrogen types in syncrudes from insitu shale oil"; Amer. Chem. Soc. Fuel. Chem. Rep.; v. 20, no. 2, p 176; 1975.
- 10. Soutar, P.S., McColgan, E.C., Merrill, W.H. and Parsons, B.I. "The hydrodesulphurization of heavy gas-oils (650-975°F) derived from Athabasca bitumen"; Mines Branch Technical Bulletin TB179; 14 p; Sept. 1973.
- 11. Williams, R.J., Draper, R.G. and Parsons, B.I. "Catalysts for hydrocracking and refining heavy oils and tars, Part 1: The effect of cobalt to molybdenum ratio on desulphurization and denitrogenation"; Mines Branch Technical Bulletin TB187; 21 p; Feb. 1974.
- 12. Ranganathan, R., Ternan, M. and Parsons, B.I. "Competing reactions in hydrotreating coker distillates from Athabasca bitumen on unpromoted and promoted catalysts"; CANMET REPORT 76-15; 16 p; Jan. 1976.

- 13. Shah, A.M., Pruden, B.B. and Denis, J.M. "Thermal hydrocracking of Athabasca bitumen effect of recycle-gas purity on product yields and qualities"; CANMET Laboratory report ERP/ERL 77-10 (R); 33 p; Jan. 1977.
- 14. Khulbe, C.P., Pruden, B.B., Denis, J.M. and Merrill, W.H. "A pilot plant investigation of thermal hydrocracking of Athabasca bitumen effect of recycle of heavy oil on product quality"; CANMET Laboratory report ERP/ERL 76-76 (R); 41 p; Aug. 1976.
- 15. Thomas, C.L. "Catalytic processes and proven catalysts"; Academic Press, New York; p 158; 1970.
- 16. Annual Book of ASTM Standards, "Petroleum products and lubricants (I)"; Am. Soc. for Testing and Materials, D396 and D975; 1974.
- 17. Montgomery, D.P. "Refining of pyrolytic shale oil"; Ind. Eng. Chem. Prod. Res. and Dev.; v. 7, no. 4, pp 274-282; Dec. 1968.
- 18. Takematsu, T. and Parsons, B.I. "A comparison of bottom-feed and top-feed reaction systems for hydrodesulphurization"; Mines Branch Technical Bulletin TB161; 18 p; Sept. 1972.
- Montagna, A. and Shah, Y.T. "Backmixing effect in an upflow co-current hydrodesulphurization reactor"; Chem. Eng. J. (Lausanne); v. 10, pp 99-105; 1975.
- 20. Specchia, V., Sicardi, S. and Gianetto, A. "Absorption in packed towers with concurrent upward flow"; A.I.Ch.E. J.; v. 20, no. 4, pp 646-653; July 1974.
- 21. Silver, H.F., Wang, N.H., Jensen, H.B. and Poulson, R.E. "A comparison of shale oil denitrification reactions over Co-Mo and Ni-W catalysts"; Am. Chem. Soc. Div. Fuel Chem. Prepr.; v. 19, no. 2, pp 147-155; 1974.
- 22. Delcos, J., Presson, R.D., Shaw, W.G. and Strecker, H.A. "Fluid-bed hydrocracking of residual stocks"; Am. Chem. Soc. Div. Petrol. Prepr; v. 11, no. 3, pp 185-191; 1966.

TABLE 1

Properties of Athabasca Bitumen and Conventional Crude Oil

	•		to the second of
		Athabasca Bitumen	Conventional Crude 0il
,		t e	4
Specific gravity, 15/15°C		1.009	0.84 to 0.9
Sulphur	wt %	4.48	0.1 to 2.0
Ash	wt %	0.59	nil
Conradson Carbon Residue	wt %	13.3	1 to 2
Pentane insolubles	wt %	15.5	-
Benzene insolubles	wt %	0.72	-
Vanadium	ppm (wt)	213	2 to 10
Nickel	ppm (wt)	67	(total metals)
Total acid number		2.77	u hose− s
Total base number	•	1.89	-
Carbon	wt %	83.36	86
Hydrogen	wt %	10.52	13.5
Nitrogen (Dohrmann microcoulometer)	wt %	0.43	0.2
Chlorine	wt %	0.00	
Viscosity at 38 ⁰ C	CSt	10,000	3 to 7
Pitch (524°C +)	wt %	51.5	1 to 5

TABLE 2

Thermal and Catalytic Hydrocracking Conditions

Thermal Hydrocracking

Pressure	MPa	13.9
Temperature	°C	450
Liquid hourly space velocity		1.0
Feed rate	g/h	4500
Temperature of hot separator	°C	450
Hydrogen	m ³ API/t	1218
Recycle Oil	g/h	9060

Catalytic Hydrocracking

Pressure	MPa	13.9
Temperature	°C	400 to 460
Catalyst loading	mL	100
Liquid hourly space velocity		1.0
Hydrogen	m ³ API/t	883

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TABLE 3

Results from First-Stage Thermal Hydrocracking of Athabasca Bitumen

Total Liquid Product		
Yield	wt %	92.3
Yield	vol %	99.7
Sulphur	wt %	2.38
Nitrogen	wt %	0.39
-524°C Distillate		• .
Yield	wt %	81.1
Sulphur	wt %	2.16
Nitrogen	wt %	0.25
Ash	wt %	0.00
Metals	wt %	0.00
+524°C Pitch		
Yield	wt %	11.2
Sulphur	wt %	4.5
Nitrogen	wt %	1.58
Ash	wt %	6.14
Metals	wt %	0.216
Pitch conversion	wt %	81.5
Sulphur removal	wt %	52.2
Nitrogen removal	wt %	17.8
Hydrogen consumed	g mol/kg feed	7.76

All yields based on feed.

TABLE 4

Properties of Oil Entering Catalytic Hydrocracking Unit

E	Boiling range	°C	IBP-510
5	Specific gravity, 15/15 ⁰ C		0.872
9	Sulphur	wt %	1.97
N	Nitrogen	ppm (wt)	1950
<u>Distil</u>	led Fractions		
<u>N</u>	Naphtha (IBP-204 ⁰ C)		
	Content	vo1 %	32.7
	Specific gravity, 15/15 ⁰ (0.768
	Sulphur	wt %	0.88
	Nitrogen	ppm (wt)	575
<u>I</u>	Light Gas-0il (204-343°C)		
	Content	vol %	46.0
•	Specific gravity, 15/15 ⁰ (0.897
	Sulphur	wt %	2.18
	Nitrogen	ppm (wt)	1404
<u> </u>	Heavy Gas-Oil (343-510 ⁰ C)		
	Content	vol %	21.3
	Specific gravity, 15/15°	C	0.991
	Sulphur	wt %	2.82
	Nitrogen	ppm (wt)	4542

TABLE 5

Properties of Product from Catalytic Hydrocracking Unit (13.9 MPa and LHSV = 1.0)

Properties		Reaction Temperature				Reaction Temperature			
	400°C	450 ⁰ C	430 ⁰ C	400°C	for typical feeds and oils				
Total Liquid Product		,							
Specific gravity, 15/15°C Sulphur wt % Nitrogen ppm (wt) Yield vol % Yield wt %	0.841 0.38 137 - -	0.812 0.15 11 99.9 93.0	0.825 0.15 15 91.3 86.4	0.839 0.17 124 97.4 92.9					
Distillate Fractions Naphtha (IBP-204°C)	***				Reformer naphtha (Ref 15)				
Content vol % Specific gravity, 15/15°C Sulphur wt % Nitrogen ppm (wt)	33.2 0.761 0.11 7	49.3 0.762 0.04 0.5	41.2 0.764 0.04 0.5	33.8 0.761 <0.04 9	- 0.002 1				
Light Gas-Oil (204-343°C) Content vol % Specific gravity, 15/15°C Sulphur wt % Nitrogen ppm (wt)	53.1 0.869 0.15 46	44.9 0.862 0.08 6	52.3 0.867 0.06 10	52.8 0.869 <0.04 65	Fuel oils (Ref 16,17) - >0.8762 <0.5 <300				
Heavy Gas-Oil (343°C +) Content vol % Specific gravity, 15/15°C Sulphur wt % Nitrogen ppm (wt)	13.7 0.924 0.28 494	5.9 0.905 0.07 91	6.5 0.901 <0.04 98	13.4 0.919 0.10	Cat-cracking gas-oil (Ref 17) <0.5 <2000 total N and <100 ppm Basic N				

TABLE 6

Comparison of Different Catalysts for Catalytic Hydrocracking

Reaction Conditions: 13.9 MPa, 460° C, 2 h⁻¹, 883 m³API/t

Catalysts Properties	3 wt % CoO-15 wt % MoO ₃ on alumina	3.8 wt % NiO-15 wt % MoO ₃ on alumina	6 wt % Ni-19 wt % W on alumina
Total Liquid Product Specific gravity, 15/15°C	0.821	0.817	0.790
Sulphur wt %	<0.04	<0.04	<0.04
Nitrogen ppm (wt)	110	110	81
Yield vol %	98.5	97.2	. 99.7
Yield wt %	92.8	91.1	90.0
Naphtha (IBP-204°C)	·		
Content vol %	45.7	49.1	64.5
Specific gravity, 15/15°C	0.763	0.762	0.757
Sulphur wt %	<0.04	<0.04	<0.04
Nitrogen ppm (wt)	16	19	8
<u>Light Gas-Oil (204-343°C)</u>			
Content vol %	51.2	48.0	32.6
Specific gravity, 15/15°C	0.871	0.865	0.853
Sulphur wt %	<0.04	<0.04	<0.04
Nitrogen ppm (wt)	47	9	3
Heavy Gas-Oil (343°C+)			
Content vol %	3.1	2.9	2.9
Specific gravity, 15/15°C	0.916	0.901	0.910
Sulphur wt %	<0.04	<0.04	<0.04
Nitrogen ppm (wt)	301	_	105

TABLE 7 Comparison of Data for Various Catalysts at 400° C, $2h^{-1}$ and for Different Reaction Times

Properties		3 wt % CoO-15 wt % MoO ₃ 3.8 wt % NiO-15 wt % MoO ₃ on alumina				6 wt % Ni-19 wt % W on alumina	
Reaction Time, h	2	12	2	12	2	12	
Total Liquid Product							
Specific gravity, 15/15°C Sulphur wt % Nitrogen ppm (wt) Yield vol % Yield wt %	0.845 0.12 369 98.6 95.6	0.841 0.16 392 99.6 96.1	0.838 0.04 86 99.6 95.7	0.841 <0.04 153 99.4 95.8	0.836 <0.04 108 99.1 95.0	0.849 <0.04 391 96.7 94.2	
Naphtha (IBP-204°C) Content vol % Specific gravity, 15/15°C Sulphur wt % Nitrogen ppm (wt)	34.6 0.763 <0.04 54	33.9 0.758 <0.04 38	39.1 0.769 <0.04 12	33.1 0.758 <0.04 5	35.9 0.761 <0.04 20	38.8 0.771 <0.04 56	
Light Gas-0il (204-343°C)							
Content vol % Specific gravity, 15/15°C Sulphur wt % Nitrogen ppm (wt)	48.9 0.876 0.06 234	52.8 0.873 <0.04 238	47.4 0.874 <0.04 17	51.2 0.869 <0.04 36	49.7 0.869 <0.04 34	43.4 0.879 <0.04 194	
Heavy Gas-Oil (343°C+) Content vol % Specific gravity, 15/15°C Sulphur wt % Nitrogen ppm (wt)	16.5 0.932 0.10 1101	13.3 0.937 0.18 1308	13.5 0.916 <0.04	15.7 0.920 <0.04	14.4 0.918 <0.04	17.8 0.939 <0.04 1083	

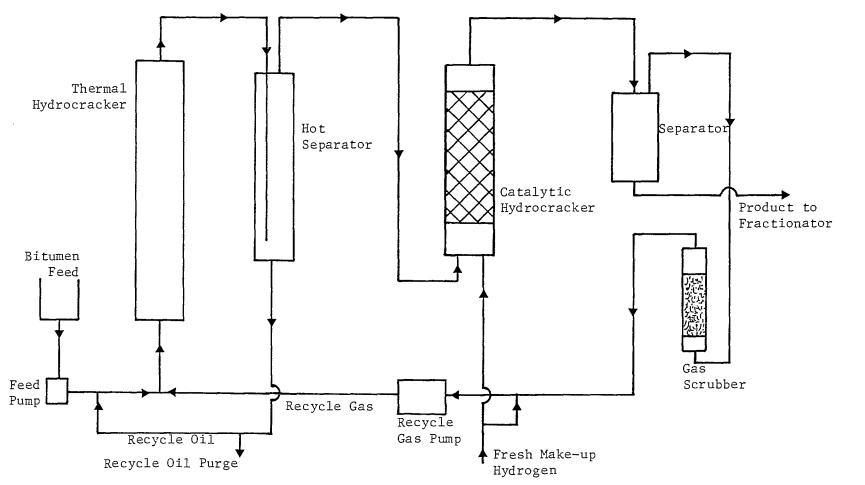


FIGURE 1 - Flowsheet for Two-stage Thermal and Catalytic Hydrocracking Process

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