

Canada Centre for Mineral and Energy Technology Centre canadien de la technologie des minéraux et de l'énergie

Energy Research Laboratories

Laboratoires de recherche sur l'énergie

EVALUATION OF LOW AND HIGH SEVERITY UPGRADING OF CANADIAN MIDDLE DISTILLATES FROM OIL SANDS AND CONVENTIONAL SOURCES

M. Skubnik, T.J. McCann and M.F. Wilson DIVISION REPORT ERL 89-18(J)
April 1989





EVALUATION OF LOW AND HIGH SEVERITY UPGRADING OF CANADIAN MIDDLE DISTILLATES FROM OIL SANDS AND CONVENTIONAL SOURCES

M. Skubnik, T.J. McCann and M.F. Wilson DIVISION REPORT ERL 89-18(J) April 1989

EVALUATION OF LOW AND HIGH SEVERITY UPGRADING OF CANADIAN MIDDLE DISTILLATES FROM OIL SANDS AND CONVENTIONAL SOURCES

M. Skubnik** T.J. McCann* and M.F. Wilson

Energy Research Laboratories, Energy, Mines and Resources Canada, 555 Booth Street, Ottawa, Ontario, K1A OG2

*RTM Engineering Ltd., #200, 6130 - 3rd Street S.E., Calgary, Alberta, T2H 1K4.

**To whom correspondence should be addressed.

Key words: Jet Fuel, Diesel Fuel, Cetane Number, Aromatics, Hydrogenation, Cost

Abstract. Future concerns for production of Canadian jet and diesel fuels for short term (1995) and long term (2005) relate to an increased supply of oil sand synthetic crudes and anticipated changes in middle distillate fuel specifications projecting sulphur and aromatic contents as low as 0.05 wt % and less than 20 vol %, respectively. The specification changes may present a formidable problem for Canadian refiners processing either synthetic or conventional crude oil. hydrogenation processes, solvent extraction of aromatics or a combination of both may be required for fuel quality improvement. A low severity route uses a supported Ni metal catalyst and a high pressure route a sulphided Ni-Mo catalyst. The Ni catalyst requires a capital intensive hydrodesulphurization/hydrodenitrogenation step bringing the feedstock sulphur and nitrogen level to 1 ppm. Considering commercial catalysts the preliminary capital costs of both routes are found to be equal or the Ni route marginally higher, but the Ni "stand-alone" route can be an economically viable process. Syncrude middle distillates hydrogenated by the Ni route can be blended at very high ratios to new specification diesel and jet fuels. development of a sulphur-tolerant nickel catalyst would greatly improve the economics of the low severity process.

INTRODUCTION

Future projections for petroleum refining in Canada indicate a decline in feedstock qualities, an increase in synthetic crude production and greater environmental constraints. In particular, middle distillate refining will be affected by the higher aromatic and sulphur contents of Canadian crudes. High levels of aromatics degrade diesel ignition and jet fuel combustion quality and may also increase engine particulate emissions [1]. Future syncrudes are expected to have somewhat lower aromatic and sulphur contents than their current levels [2], but the middle distillate aromatics will still be higher than those of conventional crudes. Thus, anticipated changes to jet and diesel fuel specifications are likely to create problems for future hydroprocessing operations in Canada. Improved hydrogenation processes, solvent extraction of aromatics or a combination of both may be required for quality improvement of future middle distillate fuels.

This paper assesses the feasibility of a low severity catalytic hydrogenation process for saturation of aromatics in middle distillates from oil sands and compares it with conventional distillate processing. The low severity process employs supported nickel metal catalysts and is based upon laboratory and pilot work carried out by CANMET/Energy Research Laboratories, Energy, Mines and Resources Canada [3-6]. The paper also compares the low severity route with "conventional"

high pressure hydrogenation using a sulphided Ni-Mo hydrotreating catalyst. The nickel catalyst route was also studied as one approach to offset the high cost of platinum used in other low pressure processes.

The paper also examines the current and future Canadian setting for middle distillate aromatics hydrogenation and notes relative economics and prospective applications for short term (1992) and long term (2005). It also identifies areas for further research and development.

ANALYSIS OF CURRENT AND FUTURE PRODUCTION OF MIDDLE DISTILLATES IN CANADA

Current situation. Current middle distillate fuel production represents about 40% of all Canadian liquid fuels. In a typical conventional Canadian refinery virgin kerosene, treated or untreated diesel fractions and light cycle oils (LCO) stabilized by hydrotreating go into a middle distillate pool. If available, hydrocracked middle distillate, which may contain a non-specification Jet A kerosene, also goes into the pool.

Some Canadian refineries have the capability to process syncrude feedstocks. Syncrude kerosene fractions typically have greater than 25 vol % aromatics and poor, 16-18, smoke points [7]. Refiners who produce Jet A fuel are therefore forced to

restrict their intake of syncrude because present specifications limit aromatics to 22 vol % (minimum allowable 25 vol %) and smoke point to 18. Syncrude diesel fractions have low cetane numbers between 30 and 35, well below the specification cetane number 40. Most Canadian refineries must also blend very low quality LCO (cetane number 25) from catalytic cracking units into diesel fuel at 10-20 vol % of the total middle distillate. To meet cetane specifications many refiners use cetane improvers which become very expensive beyond a 5 to 6 cetane number increase. To meet current jet fuel aromatic and diesel fuel cetane number specifications a conventional refinery is restricted to an intake of syncrude to maximum 15 vol % of its capacity.

Future concerns. The National Energy Board forecasts only a modest increase of 19% in total Canadian crude oil demand from 1985 to 2005 [8]. However, for the same period, production of syncrude may increase by 42% for low and by 115% for high cost scenarios. Demand for future middle distillate fuels may also increase to 44% by 1995 and reach 45% by 2005 [2]. Intake of crude oils which yield high amounts of middle distillates rich in aromatics poses a major processing challenge for production of specification jet and diesel fuels and may affect adversely regional demands for gasoline to middle distillate production ratios.

specification changes. Specifications of 0.05 wt % sulphur and a 20 vol % aromatics have been proposed for diesel fuels in the U.S. to meet 1995 engine emission standards [9]. In Canada the odds for gradual implementation of new sulphur and aromatic specifications by 1996 are high [10]. Specific evidence, which correlates aromatic and other fuel parameters with engine emissions, will be available as early as mid-1989. Table 1 shows a preliminary estimate of Canadian middle distillate specification changes between 1987 and 1996.

More stringent middle distillate fuel specifications for aromatic and sulphur contents may require installation of aromatics reduction units for syncrude processing plants and desulphurization units for conventional crude oil refineries. Because the fuel standards are relevant to new engines which are designed and built in the U.S. it is generally agreed that Canada will closely follow the U.S. standards.

Aromatics hydrogenation capabilities of Canadian refineries. Only a few Canadian syncrude processing refineries and one oil sands upgrading plant have significant capabilities for aromatics hydrogenation of middle distillates. Shell Canada Ltd. at Scotford, a syncrude dedicated refinery, hydrogenates a part of straight and all hydrocracked middle distillate over a platinum catalyst to specification jet and diesel fuels [11]. Petro-Canada

Products Inc., Edmonton and Suncor Inc., Sarnia have a 35% and 90% intake capability of syncrude, respectively. Since 1983 Petro-Canada has been operating a mild hydrocracking unit for hydrogenation of a blend of syncrude middle distillate with LCO [12]. This unit also operates in a block mode as a hydrocracker for conversion of syncrude gas oil into high quality diesel products. For middle distillate from heavy oil upgrading a similar mild hydrocracking unit has been recently put into operation at New Grade in Regina.

Imposition of new specifications for diesel fuel aromatics ranging from 20 to 25 vol % would necessitate the installation of hydrogenation units in about 12 Canadian refineries. The introduction of new hydrogenation capacity at one or both existing oil sands bitumen upgrading plants in Alberta could displace up to four of these units in downstream operations. Nevertheless, aromatic hydrogenation in virgin and syncrude distillates, some hydrocracked distillates (especially where syncrudes are processed) and a catalytically cracked LCO may all be required. To ease Jet A fuel production problems due to syncrude and other future high aromatic crudes, additional kerosene hydrogenation units may also be needed. Thus a significant Canadian market is foreseen for aromatic

Canada. In the short term, to 1995, up to three kerosene units are possible, and in the long term, beyond 1995, another five diesel units are likely with the introduction of a new aromatics specification.

ALTERNATIVES FOR MIDDLE DISTILLATE UPGRADING

Considering the above analysis one may assume that new aromatic hydrogenation facilities are likely to be needed in Canada by 1996. An alternative processing route, which could be used in isolated cases, is solvent extraction. Recent work has explored the possibility for combined aromatics hydrogenation and extraction [5]. However, in virtually all situations involving extraction, disposal of the aromatic extract presents a major problem.

The following are six hydroprocessing alternatives based on the type of catalyst used, a major determinant of process conditions:

Platinum sulphide catalyst (Type I). In this process the feedstock sulphur is converted to H₂S before passing through a bed of platinum sulphide. The latter hydrogenation stage operates at 6.9 MPa but at higher temperatures than are needed for hydrogenation over platinum (Type II) and nickel (Type III). In spite of some hydrocracking the product yield is still about 100 %. The ability to handle feeds up to 10,000 ppm sulphur is claimed.

supported platinum metal catalysts (Type II). Commercially available platinum catalysts require sulphur levels below 15 ppm [13]. It is anticipated that a newly developed 150 ppm sulphur-tolerant catalyst could enter the market within two years. Current processes operate at 5.0 MPa and below 200°C [14]. Shell's syncrude middle distillate hydrogenation unit at Scotford falls into this category. Virtually all platinum catalysts are regenerable and sulphur and nitrogen are temporary poisons only.

Supported nickel metal catalysts (Type III). Commercial nickel catalysts are very competitive with platinum for hydrogenation of feedstocks containing less than 2-3 ppm sulphur. Nickel catalysts are not regenerable and sulphur accumulates as a poison [13]. Guard beds of special disposable nickel "adsorbents" placed in front of high activity nickel (or platinum) catalysts can considerably extend, at a cost, their life cycle. Operating conditions for nickel catalysts are very similar to those for platinum. Nickel catalysts have also been used in a slurry mode for benzene hydrogenation. In one commercially available catalyst, copper and cobalt slightly improve the sulphur tolerance and reduce the hydrocracking tendencies of pure nickel.

Conventional sulphided Ni-Mo and Ni-W catalysts (Type IV).

Hydrotreating catalysts are used for aromatic saturation and operate between 340°C-380°C with both minimal hydrocracking and thermodynamic , equilibrium effects on aromatics conversion [3,15,16]. Hydrogen pressures range from 10 to 20 MPa. In spite of significant sulphur and nitrogen tolerance, a dual catalyst or high temperature sulphided Co-Mo hydrotreating reactor unit may be required for high sulphur-containing feed stocks. All catalyst types in this group are regenerable and are the least expensive of hydroprocessing catalyst types.

Mild middle distillate hydrocracking catalysts (Type V). This group includes Type IV catalysts, or specifically formulated sulphided metal catalysts with added fluoride and other promoters on a silica-alumina support. The process operates above 400°C and at hydrogen pressures between 12.2 and 13.6 MPa. This operation gives lower yields of middle distillates ranging from 92 to 94%, but enhances cetane number through cracking of partially saturated polycyclic compounds in the feed to lighter monoaromatics and paraffinic products [17]. The middle distillate yield is recovered as good quality naphtha. As mentioned, two mild hydrocracking units for improving syncrude middle distillates have been installed in Gulf/Chevron and Unocal are the major promoters of this Canada. approach.

Newly developed catalysts (Type VI). These are hydrogenation catalysts which were adapted for petroleum refining after they proved successful in other industries. These proprietary, often trimetallic catalysts incorporate high activities for desulphurization (cobalt) and the hydrogenation capabilities of other metals usually in association with molybdenum.

Generally, as one follows through from Type II to Type V processes the capital cost increases as pressure and temperature rise. However, the sulphur tolerance also rises markedly. In Canadian middle distillate scenarios the lack of sulphur tolerance of platinum and nickel metal catalysts necessitates an in-depth hydrodesulphurization (HDS) of the feedstock.

To date, aromatics hydrogenation remains the most viable route for the short and long term Canadian middle distillate situation. The following sections give a preliminary assessment and comparison of two hydrogenation processes: the first uses a Type IV catalyst in a "conventional" Ni-Mo route and the second a Type III catalyst in a low severity Ni route.

TECHNICAL AND COST COMPARISON OF LOW SEVERITY NI ROUTE AND HIGH SEVERITY NI-MO ROUTE FOR HYDROGENATION OF MIDDLE DISTILLATES

Terms of reference and process arrangements.

<u>Selected Canadian middle distillate feedstocks</u>. Four Canadian feedstocks were selected to compare the low and conventional high severity processes. They cover the range of middle distillates which Canadian refiners would normally expect to process:

- (1) Suncor Inc. kerosene this feedstock boils marginally higher than conventional kerosene 190°C 340°C). The jet fuel fraction generally has an aromatic content from 23 to 30 vol % which does not meet the product specification, and hence the Jet A smoke point is below standard. Suncor kerosene cetane number of about 35 is well below the specification of 40. The feedstock considered for this study had 200 ppm sulphur and 30 vol % aromatics.
- (2) Syncrude Canada Ltd. middle distillate this feedstock currently represents the largest output of synthetic middle distillate from oil sands. The quality is sufficiently low to justify construction of additional hydroprocessing units for improving jet and diesel fuel fractions. The feedstock is expected to increase in availability by 50 to 70% over the next 10 years. As mentioned, recently Syncrude added a single hydrotreater

unit for improvement of a portion of middle distillates. However, the quality of the distillate may improve in the mid 1990's if added deep hydrotreating is installed as part of a major expansion. It is assumed that the feedstock has 400 ppm sulphur and 36 vol % aromatics.

- (3) Blend of virgin diesel (70%) and light cycle oil (30%) if a stringent diesel aromatic specification is imposed, it is expected that this blend would become the major feedstock requiring aromatics hydrogenation in Canada. In this study the distillate is assumed to contain up to 2000 ppm sulphur and 41 vol % aromatics.
- (4) Light cycle oil this is the poorest quality feedstock considered. In an average Canadian refinery with a catalytic cracking facility, the availability represents only about 20% of total middle distillates processed hence a smaller hydrogenation unit is deemed appropriate for the purpose of the study. A feedstock containing 3000 ppm sulphur and 70 vol % aromatics is considered.

In cases (3) and (4), existing low pressure hydrotreating units have been assumed available. These units provide bulk desulphurization to 2000 - 3000 ppm and olefin saturation at lower costs than if performed in hydrotreaters attached to aromatic hydrogenation reactors. Aromatic and sulphur contents of all four feedstocks are shown in Tables 2 and 3.

Product quality. A product quality target of 20 vol % total aromatics and 0.05 wt % sulphur is assumed in all cases. Since the Ni route has sufficient activity to generate a product with a much lower aromatic content, to minimize costs for both syncrude distillates, in most cases a portion of the feed is assumed to bypass the hydrogenation reactor. Such an arrangement allows some polycyclic aromatics to enter the final product. There is some evidence that nickel catalysts could tolerate higher than 1 ppm each of sulphur and nitrogen [6]. However, in this analysis all four Ni route cases have the necessary facilities to lower both catalyst poisons to 1 ppm either from the total feed or from streams passing only through the hydrogenation reactors. No cost credit has been given to products containing less than <0.05 wt % sulphur.

General process arrangements. The study considers a throughput of 2000 m³/d for feedstocks (1) through (3). A throughput of 1000 m³/d would better suit the scenario for the LCO feedstock. The number of reactors and catalyst beds varies. In principle, the temperature of reactors is controlled by a cooled quench gas in the conventional Ni-Mo route and by a cooled liquid recycle in the low severity Ni route. The process battery limits are delineated by feedstock pump systems, make-up hydrogen compressors and facilities for product recovery.

Based on the different sulphur-tolerant catalysts, complete middle distillate upgrading can be accomplished in one reaction stage for the Ni-Mo route but in two stages - sulphur/nitrogen removal and aromatics hydrogenation - for the Ni route. Only in cases with a very low sulphur content can a stand-alone Ni route be used as demonstrated below.

Comparison of low and high severity hydrogenation processes.

Conventional high severity process (sulphided Ni-Mo catalyst).

Table 2 summarizes the principal operating parameters for each feedstock case for a process based on sulphided Ni-Mo catalyst, e.g., Katalco NM-506 or equivalent. Table 2 also gives details of sulphur and aromatic contents of feedstocks and products. It should be noted that as the compositions of the feedstocks change from light Suncor kerosene to LCO, the aromatics hydrogenation and hydrotreating severities increase. Consequently, the process severity expressed in terms of liquid hourly space velocity (LHSV) varies from 2.0 to 0.8, the reactor temperature from 280 to 335°C and the pressure from 10.1 to 15.2 MPa.

Apart from reactors with specially designed multiple catalyst beds and recycle gas quench systems for close temperature control the Ni-Mo route shown in Fig. 1 would be identical to any commercial hydrotreating process. The number of reactors and catalyst beds varies, which is indicative of the

high exothermic heat of aromatics hydrogenation, particularly with LCO.

Low severity process (nickel catalysts) with HDS/HDN. Table 3 summarizes for each feedstock, the principal parameters for both process stages. Stage 1 is a (HDS/HDN) reactor utilizing a sulphided Co-Mo catalyst (Akzo Chemie 742 or equivalent). Stage 2 is the aromatics hydrogenation and employs a Ni/SiO2-Al2O3 supported catalyst (Harshaw Ni-3288 or equivalent). Table 3 also gives the reactor system throughput and bypass for each feedstock and the number of reactors for each stage. Also shown are the aromatic and sulphur contents of the feedstocks and of the intermediate and final products. The process parameters do not vary significantly. For the HDS/HDN stage, the LHSV varies between 0.8 and 2.0, the temperature from 349°C to 366°C and pressure from 8.4 to 10.5 MPa. For the hydrogenation stage, the LHSV varies between 4.0 and 1.5, the temperature from 160°C (start of run) to 250°C (end of run) and pressure from 3.2 to 4.2 MPa.

Compared with the conventional Ni-Mo route presented above, the two-stage Ni route is more complex. The HDS/HDN stage (Fig. 2) is similar to the Ni-Mo route, but operates at lower pressure and with reduced catalyst inventory. The hydrogenation stage includes guard bed reactors operating in the liquid phase between 160°C and 220°C and in the absence of hydrogen. With the exception of Suncor kerosene, in all cases hydrogenation features a feed split between multiple reactors. The hydrogenation

reactor temperature is controlled by the cooled liquid recycle as shown in Fig. 2. For this study, fixed bed hydrogenation reactors are considered, but for better temperature control slurry or ebullated bed reactors may be useful.

Nitrogen and water are nickel catalyst poisons at approximately 1 ppm, hence efficient denitrogenation and water stripping are required in the first stage. To remove most of the sulphur the sulphided Co-Mo catalyst has to operate at relatively high temperatures at which traces of olefins may form. formed organic sulphur compounds resulting from a recombination of olefins with H₂S may pass through the stripper. It is therefore assumed that the product from the HDS/HDN stage contains 5 ppm sulphur. To maintain the life of the nickel catalyst for a reasonable period, guard beds are inserted in front of the hydrogenation reactors. Fresh and deactivated nickel catalysts have significant capacity to capture organic sulphur compounds. However, a spent nickel catalyst cannot be a self-sustained sulphur adsorbent since it "bleeds" through a portion of sulphur from the HDS/HDN stage. The study considers the use of an adsorbent, Harshaw Ni-0750, a cheaper version of the hydrogenation Ni catalyst, or equivalent. This adsorbent retains about 10 times as much sulphur as the fresh nickel catalyst. It is capable of removing completely organic sulphur compounds from the HDS/HDN stage product. Use of the spent Ni hydrogenation catalyst for capture of residual sulphur in series prior to the above adsorbent could however reduce total costs.

Stand-alone Ni route. In some refinery operations, kerosene streams which are hydrotreated along with naphtha may yield kerosene products with maximum nitrogen and sulphur levels of approximately 1 and 10 ppm respectively. Kerosenes from hydrocracking of syncrude heavy gas oils have about the same levels of sulphur but higher amounts of nitrogen. These kerosenes can have aromatic contents up to 30 vol % and are not necessarily acceptable as Jet A fuel products. The aromatics could be reduced to a very low level in a modified Ni route process without HDS/HDN provided the excess feed sulphur is removed by a nickel adsorbent in multiple guard beds.

Figure 3 shows the modified Ni route process without HDS/HDN. For a feedstock containing 10 ppm sulphur and 30 vol % aromatics the study considers a reactor system throughput of 800 m³/d and a final kerosene product output of 2000 m³/d with lower than 20 vol % aromatics. A third guard bed has been added in addition to the two units employed in the above case with prior HDS/HDN.

COST COMPARISON OF HIGH AND LOW SEVERITY PROCESSES

Ni-Mo route versus Ni route. Cost estimates for the four middle distillate feedstock cases applied to the two process routes are based on 1987 Western Canadian prices. The estimates omit a slightly lower liquid yield for the Ni route caused by the higher temperature of the HDS/HDN stage which leads to more hydrocracking. Also the hydrogen demand for the Ni route is

slightly higher due to additional losses in gas/liquid separation in the hydrogenation step.

Table 4 presents cost comparisons for the Ni-Mo and Ni routes. In all feedstock cases studied, the capital costs of the Ni route are more or less equal to Ni-Mo. However, the operating costs are marginally higher due to the non-regenerability of the nickel catalyst, marginally poorer energy efficiency and greater process complexity. It is important to note that the major expenses of the Ni route lie in the HDS/HDN stage which carries approximately 75% of the capital and 65% of the operating costs (exclusive of hydrogen make-up costs).

Current (1987) prices of the non-regenerable, low sulphur and low nitrogen tolerant nickel catalyst and the nickel-based sulphur sorbent are about \$37 and \$27/kg, respectively. It is believed that price reduction due to increased production volumes of both the nickel catalyst and the adsorbent would significantly improve the economic feasibility of the Ni route. Other factors having a positive effect would be improved sulphur and nitrogen tolerance and catalyst regeneration.

The capital cost estimates of the study case for light cycle oil hydrogenation, a 1000 m³/d throughput unit, was compared with a similar estimate made for the AH Unibon process provided by UOP Inc. This is a similar unit using a platinum catalyst. A small difference (5%) in the cost estimates for nickel and platinum was found and confirmed the adequacy of the methods used in this study.

Cost of the stand alone Ni route. Including costs for the nickel catalyst and adsorbent the estimated capital costs of a 2000 m³/d stand-alone unit for processing low sulphur feedstocks is estimated at \$10 million and operating costs, exclusive of hydrogen make-up costs, at \$2.1/m³ (Table 4).

CONCLUSIONS

Figure 4 provides a simplified overview of the "fit" of various middle distillate aromatics hydrogenation routes as developed in this study of four representative Canadian feedstocks. The work concludes that a low severity hydrogenation route using certain types of commercial nickel catalysts will be competitive with platinum for distillate aromatics conversion when feedstock sulphur is below 5 ppm. In certain circumstances a nickel route will also be competitive with platinum in the 5 to 15 ppm range with enhanced guard beds. When the feedstock sulphur level is above 5000 ppm and an HDS/HDN stage is required by all available routes, the nickel route may compete effectively with sulphided Ni-Mo and Ni-W catalysts. All hydrogenation routes are very capital intensive especially above 15 ppm sulphur, with about 75% of the capital costs for Pt and Ni routes being in the HDS/HDN stage.

The ability of mild middle distillate hydrocracking to improve cetane number beyond that possible through aromatics

hydrogenation alone is to be noted. However, the mild hydrocracking route may not provide enough aromatics saturation to attain Jet A or future diesel fuel aromatic specifications. The requirement for installation of new aromatics hydrogenation plants in Canada by 1996 will be determined by the imposition of a new aromatic specification for jet and diesel fuels.

It is important to note the major role which sulphur tolerance plays in the selection of an aromatics hydrogenation process. The non-regenerability of current nickel catalysts is also a major disadvantage. There is a need to investigate optimum HDS/HDN conditions and catalysts to determine if the high capital costs of this stage can be reduced.

Syncrude middle distillates hydrogenated over a nickel (or a noble metal) catalyst produce sulphur-free fractions with very low contents of aromatics [4-6]. These fractions could be blended at very high ratios with untreated or desulphurized conventional middle distillates to meet anticipated new specifications for diesel and jet fuels. Installation of the Ni process could considerably increase utilization of Canadian syncrudes by conventional refiners well above the current level.

ACKNOWLEDGEMENT

The authors wish to thank the team of RTM Engineering Ltd. and associated companies for their contributions in carrying out this study.

REFERENCES

- 1. M.F. Wilson, "Impact of Excessive Aromatics in Oil Sands Syncrudes on Production and Quality of Middle Distillate Fuels", CANMET Report 82-2E (1981).
- 2. J.E. Devai, "The Canadian Refining Industry Outlook for the Future", Paper 64C, AICHE National Meeting, Houston (1987).
- 3. M.F. Wilson, I.P. Fisher, and J.F. Kriz, Journal of Catalysis, 95 (1985) 155.
- 4. M.F. Wilson, I.P. Fisher, and J.F. Kriz, Industrial and Engineering Chemistry Product Research and Development, 25 (1986) 505.
- 5. M.F. Wilson, I.P. Fisher and J.F. Kriz, Energy and Fuels, 1 (1987) 540.
- 6. M.F. Wilson, P.R. Mainwaring, J.R. Brown and J.F. Kriz, Applied Catalysis, 41 (1988) 177.
- 7. D.E. Steere, W.A. MacDonald and D.H. Stone, "Characteristics of Fuel Products from the Canadian Tar Sands", API, 46th Midyear Refining Meeting, Chicago, Ill. (1981).
- 8. Canadian National Energy Board, "Canadian Energy Supply and Demand 1985-2005", Supply and Services Canada, Ottawa, Ontario (1986).

- 9. D.C. McCullough, M.D. Edgar, and J.T. Pistorius, "Higher Severity Diesel Hydrotreating", NPRA Annual Meeting, San Antonio, Texas (1987).
- 10. J.R. Yoes, and M.Y. Asim, "Confronting New Challenges in Distillate Hydrotreating", NPRA Annual Meeting, San Antonio, Texas (1987).
- 11. D.M. Simpson, International Journal of Hydrogen Energy, 9 (1984) 95.
- 12. L.W. Brunn, N.E. Kaparakos, R.W. Plesko, and B.E. Schoenroth, Oil Gas Journal, 82 (1984) 90.
- 13. C.H. Bartholomew, P.K. Agarwal, and J.R. Katzer, "Sulphur Poisoning of Metals", Advances in Catalysis, 31 (1982) 135.
- 14. D.D. Cobb, and D.G. Chapel, Oil & Gas Journal, 83 (1985) 60.
- 15. M.F. Wilson, J.F. Kriz, Fuel, 63 (1984) 190.
- 16. M.F. Wilson, J.F. Kriz, Fuel, 64 (1985) 1179.
- 17. F.O. Hill and R.E. Peterson, "Hydrogenation Process Solves Cracked Distillate Quality Problems", AICHE Spring National Meeting, Anaheim, California (1982).

Table 1 - Anticipated changes in Canadian middle distillate fuel specifications

7

Product	•	Year		
	Component 	1987	1992	1996
Road diesel fuel	Sulphur, wt %	0.5(^a)	0.15	0.05
	Aromatics, vol %	(b)	(b)	>20 (°)
	90% point, °C	360	360	340
Railway diesel fuel	Sulphur, wt %	(b)	0.15	0.05
Jet fuel type A,	Sulphur, wt %	0.2	0.1	0.05
A1 and A2	Aromatics, vol %	22(d)	22(^e)	>20(^e)
Light fuel oil No. 2	Sulphur, wt %	0.5(^a)	0.15	0.05(^f)

- (a) An internal refinery specification is generally in use in Canada.
- (b) No standard.
- (c) May be stated as the equivalent of alkylbenzenes with a penalty for polynuclear aromatics.
- (d) Can be used with notification up to 25 vol % aromatics.
- (e) No allowance above 22 vol % aromatics.
- (f) A combustion quality specification may be added to reduce aromatic content.

Table 2 - Conventional Ni-Mo route hydrogenation process parameters

Feedstock		middle distillate	Blend of conv. diesel oil & LCO	
Feed rate, m ³ /d	2000	2000	2000	1000
Sulphur in/out,	200/<100	400/<200	2000/<500	3000/<500
Aromatics in/out,	30/20	36/20	41/20	70/20
LHSV	2.0	1.5	1.0	0.8
Average reactor temperature, °C	280	280	315	335
Pressure, MPa	10.1	11.5	13.1	15.2
Catalyst	Katalco Ni or equiva	·	or Shell 4545	(Ni-W)

Table 3 - Low severity Ni route hydrogenation process parameters

Feedstock	Suncor kerosene	Syncrude middle distillate	Blend of conv. dieseloil & LCO	LCO
Total feed rate, m ³ /d	2000	2000	2000	1000
Reactor system				
throughput, m ³ /d	800	1100	2000	1000
bypass, m ³ /d	1200	900	0	0
Hydrodesulphurization/hydrod	<u>enitrogena</u>	tion stage		
Sulphur in/out, ppm	200/5	400/5	2000/5	3000/5
Aromatics in/out, vol %	30/30	36/36	41/41	7 0 /70
LHSV	2.0	1.5	1.2	0.8
No. of reactors	1	1	1 or 2	2
SOR(^a) reactor temperature,	°C 349	354	354	354
EOR(^b) reactor temperature,	°C 360	366	366	366
Pressure, MPa	8.4	10.5	10.5	10.5
Catalyst Co-Mo	on alumina	- Akzo 742,	or equivalen	t
<u>Hydrogenation_stage</u>			·	
Sulphur in/out, ppm	<5/0	<5/0	<5/0	<5 /0
Aromatics in/out, vol%	30/5	36/5	41/20	7 0 /20
LHSV	4.0	3.0	3.0	1.5
No. of reactors	1	2	2	3
SOR(^a) reactor temperature,	°C 160	170	170	170
EOR(b) reactor temperature,	°C 250	250	250	250
Pressure, MPa	3.2	4.2	4.2	4.2
Catalyst Ni on	silica alu	ımina – Harsh	aw Ni-3288 or	
equiva	lent			

⁽a) SOR - start of run

⁽b) EOR - end of run

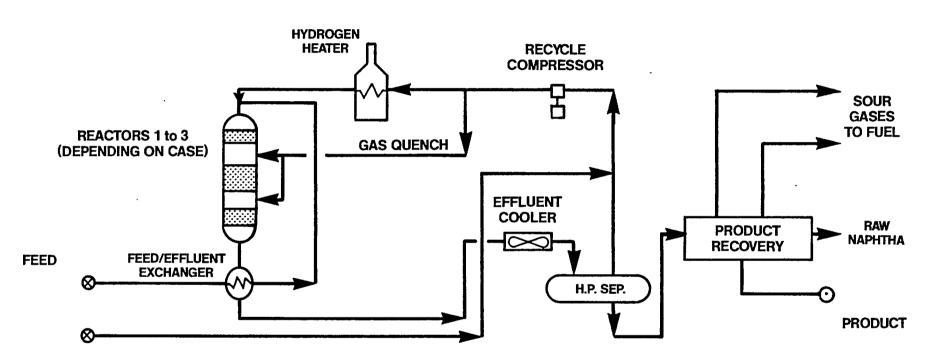
Table 4 - Cost comparison of Ni-Mo and Ni routes (1987 Canadian dollars)

Feedstock	Kerosene		middle	Blend of conv. diesel oil & LCO(a)	LCO
Total feed rate, m ³ /d	2000	2000	2000	2000	1000
	Capi [†] 	tal costs, :	\$10 ³ /m ³ /d		
Ni-Mo route	_	10.2	12.0	14.8	29.5
Ni route	-		13.2	17.2	
Ni stand-alone route	10.0	-	-	-	_
	0pera 	ating costs,	, \$/m ³ (^a)		
Ni-Mo route	-	2.6	2.7	3.6	3.5
Ni route	-	3.2	4.1	6.2	5.6
Ni Stand-Alone route	2.1	-	-	_	_

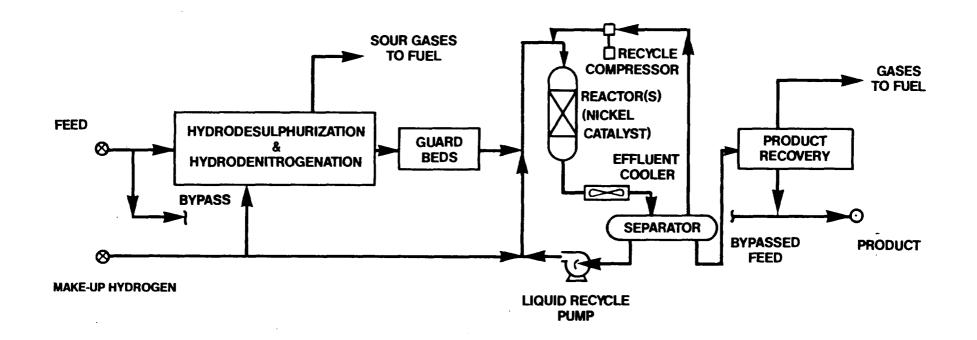
⁽a) Operating costs exclusive of hydrogen make-up costs

FIGURE CAPTIONS

- Simplified flow diagram of a conventional aromatics hydrogenation process using a sulphided Ni-Mo catalyst.
- 2. Simplified flow diagram of a low severity aromatics hydrogenation process using a supported Ni catalyst combined with HDS/HDN step.
- 3. Simplified flow diagram of a stand-alone aromatics hydrogenation process using a supported Ni catalyst.
- 4. Approximate economic "fit" of middle distillate aromatics hydrogenation processes.



MAKE-UP HYDROGEN



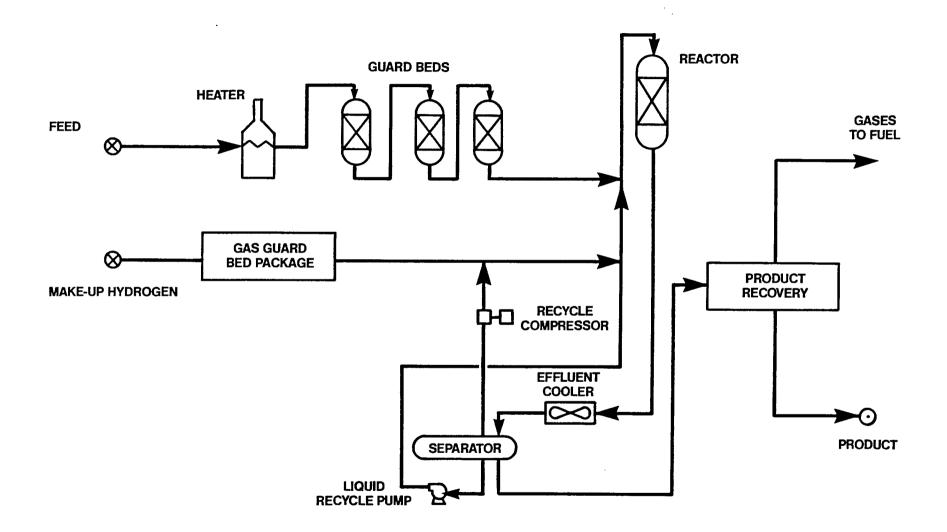
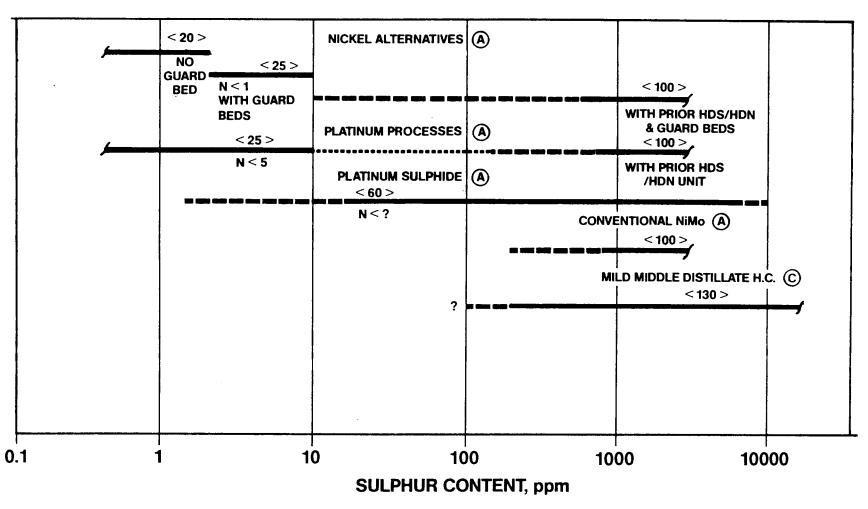


FIG.3



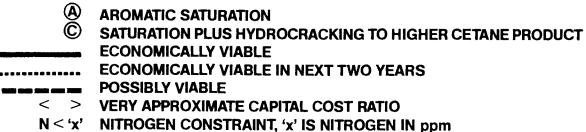


FIG. 4