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EFFECTS OF CATALYTIC HYDROPROCESSING ON MIDDLE
DISTILLATES FROM ATHABASCA SYNCRUDES

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NOVEMBER 1984

ERP /ERL 84-57 (J)

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ABSTRACT

A series of fuel products was generated by secondary hydrotreating a middle distillate fraction cut from a synthetic crude oil produced by fluid-bed coking of Athabasca bitumen. The reactions were carried out over a sulphided nickel-tungsten on alumina catalyst at severe operating conditions. The ignition quality of fuel products was determined by a series of tests using a standard cetane engine. Jet fuel combustion quality was evaluated by means of a standard smoke point test. The compositional analyses of the fuels were determined by low-resolution mass spectrometry and aromatic carbon content by ^{13}C n.m.r. Fuel product ignition and combustion properties were related to the concentrations of aromatics and compared with similar relationships obtained for distillates from delayed coking of bitumen. A method for the determination of hydrogen consumption by mass spectrometry is described and the amount of hydrogen consumed during reaction is correlated with the degree of cetane improvement. The effectiveness of fuel quality enhancement by aromatics saturation is discussed with reference to an alternative upgrading procedure involving ring-opening of naphthenes.

INTRODUCTION

In recent years, increased activity in the production of synthetic crudes from a variety of natural resources has led to the development of unique transportation fuels. Because of their unusual chemical compositions and often correspondingly poor qualities, such fuels place greater demands on conventional engine combustion processes. To some extent these problems have stimulated a greater drive towards developing new engine designs to accommodate poorer quality fuels, but a great deal of the effort needed will be in distillate refining and this will mean the development of new processes.

With future developments concerning the production of synthetic crudes from heavy oils, oil sands and coal, it is expected that primary upgrading processes will continue to yield middle distillates which are low in paraffins and relatively high in aromatics and naphthenes. The simplest approach for correcting the imbalance of saturates and improving the ignition and combustion qualities of these potential transportation fuels (jet and diesel) is to input hydrogen by conversion of aromatics to naphthenes. However, as discussed below, some arguments against the use of this particular processing solution have also been raised.

An aspect which appears somewhat obscure and neglected is our knowledge of the combustion processes and a greater understanding is needed of how fuels of diverse compositions affect the mechanisms of combustion and lead to reduced efficiency in engine performance.

An examination is made of some of the relationships found between fuel aromaticity and ignition and combustion properties. The efficiency of hydroprocessing on fuel quality improvement is also evaluated in terms of hydrogen consumption. Since doubts arise concerning the effectiveness of current processing methods some attempt is made to identify new research areas.

EXPERIMENTAL

The feedstock was a middle distillate fraction cut from a synthetic crude oil produced by fluid-bed coking of Athabasca bitumen (synthetic crude A).Properties of the feedstock are presented in Table 1. Samples of fuel products were generated by secondary hydrotreating the feed over a sulphided commercial $NiO-WO_3/\gamma-Al_2O_3$ catalyst (Katalco Sphericat NT-550) evaluated in a previous study[1].

A detailed description of the bench-scale hydrotreating system was presented earlier[2]. Hydroprocessing runs were carried out using 70 g of catalyst in 100 cm^3 of

reactor volume. The catalyst sulphiding procedure was given earlier[1]. The continuous flow reactor was operated in the up-flow mode, the liquid feed and hydrogen were mixed, passed through a pre-heater, then over a fixed catalyst bed. Experimental runs were carried out from 340 to 440°C, liquid space velocities of 0.75-2.00 h^{-1} and hydrogen pressures of 7.00-17.3 MPa (500-2500 psig). A hydrogen flowrate at STP of 530 dm^3 (hydrogen) dm^{-3} (feedstock)(3000 scf bbl^{-1}) was maintained and hydrogen gas was vented without recycle. The reactor system was operated at steady state for 1 h prior to the period in which fuel product was collected.

Compositional analyses of the fuels were performed using low resolution mass spectrometry. A Consolidated Electrodynamics Corporation Model 21-103C mass spectrometer fitted with a Micro-Tek vacuum lock introduction system was interfaced with a Modular Computer Systems Inc. Modcomp II/221 for logging the spectra and data reduction. The hydrocarbon group type compositions of the samples were determined by a modification of the method originally developed by Robinson[3]. This method requires no separation of the sample into saturate and aromatic fractions. The aromatic carbon content was obtained by ^{13}C n.m.r. analysis using a Varian XL-200 spectrometer. GC/MS spectra were determined by means of a Kratos Inc. MS.25 instrument utilizing a Carlo-Erba GC. A 25 m capillary column with methyl silicone stationary phase was used with

helium as carrier gas. The instrument was interfaced with an Eclipse S120 computer using a DS55 data system. Cetane numbers of fuel product samples were determined by means of an engine test. Determinations were made with a standard Cooperative Fuels Research test engine using a constant compression ratio method. Jet fuel combustion quality was evaluated by means of a standard smoke point test.

RESULTS AND DISCUSSION

Effects of secondary hydrotreating on fuel product compositions

The present work employs mass spectrometry to identify a number of different hydrocarbon group types in middle distillate products. The analytical method is based on the classification of hydrocarbons according to ring structure and degree of saturation[3]. The technique effectively distinguishes four saturated group types including paraffins and cycloparaffins, and a series of aromatic groups which covers mono-, di- and tri-aromatics. Figure 1 presents summarized chemical changes for conversion of some of the aromatic group types to their corresponding naphthenes. The various ring compound types shown are identified by z number which is a measure of the hydrogen deficiency of each species (see below).

The amount of each hydrocarbon group type in a distillate product is essentially determined by the

feedstock composition and by the processing conditions used in hydrotreating. Table 2 presents examples of fuel product compositions from secondary hydrotreating and processing conditions. The compositional analysis of the feedstock is included as well as corresponding aromatic carbon contents (determined by [13]C n.m.r.) and cetane numbers of the fuels. The processing conditions cover a wide range of temperatures and pressures and results indicate that a carefully chosen optimum temperature of 380°C is required as well as severe operating pressures, at least 14 MPa, to achieve the required diesel fuel ignition specification, i.e., cetane number 40. The optimum operating conditions coincide with those of previous work for upgrading middle distillates from delayed-coked bitumen[1].

Examination of the fuel compositions in Table 2 for various processing conditions shows some of the effects of temperature and pressure. It is noted that concentrations of aromatics are affected by the shift of thermodynamic equilibrium. High temperatures and low pressures favour the formation of aromatics. These effects were discussed in detail previously[1].

At the optimum hydroprocessing conditions, the compositional analyses also show that, essentially, almost complete conversion of aromatics to naphthenes is required to produce specification diesel fuel. Thus experimental condition 3, producing fuel of cetane number 42.5,

indicates only residual levels of benzocycloparaffins, benzodicycloparaffins and naphthalenes. The low 0.2% level of naphthalenes may in fact be due to an intrinsic analytical error. Total saturates in the fuel is 98.8%.

For fuel compositions 1 to 4, other effects to be noted are a steady small increase in paraffin content with increasing temperature which is due to cracking and maxima in cycloparaffin content at 380°C which, together with the ^{13}C n.m.r. results, confirm the thermodynamic equilibrium effect.

Interrelation of fuel aromaticity with ignition and combustion properties

Relations were established previously between aromaticity (determined by ^{13}C n.m.r.) and fuel properties for distillate from a synthetic crude produced by delayed coking of Athabasca bitumen, i.e., synthetic crude B (Table 1)[1]. These relations are explored further by comparison with a distillate from synthetic crude A.

Figure 2 shows plots of per cent aromatic carbon (% C_a) versus cetane number for fuel products from both distillates and shows the aromatic carbon contents and cetane numbers of both feedstocks with the current Canadian diesel fuel specification (cetane number 40, indicated by a broken line).

Figure 2 reveals qualitative differences between middle distillates from syncrudes A and B. For any aromatic carbon content, the syncrude produced by delayed

coking of bitumen gives a distillate of superior cetane
rating. Examination of the compositions of distillates
from these syncrudes before and after secondary hydro-
treating reveals that distillate from syncrude B is always
significantly higher in paraffins and this almost
certainly accounts for the better fuel ignition quality.

We attribute the curvatures of the plots in Figure 2
to the presence of various aromatic carbon types of
different reactivities which determine their resistance to
hydrogenation and combustion more or less equally. Thus
under relatively mild hydroprocessing conditions, a
significant percentage of the total aromatic carbon
content may easily be converted but this may have little
effect on the fuel ignition quality. As processing
severities are increased, more stable species are satura-
ted but it appears that the largest gains in cetane
improvement are made only after the greater portion of
aromatic carbons are converted. This suggests that
relatively small amounts of certain aromatic carbon types
can affect adversley the diesel ignition quality, or that
real gains in cetane number are made when small amounts of
good quality paraffins are formed by cracking.

Examples of aromatic hydrocarbon group types whose
primary conversion to hydroaromatics is expected to make

little impact on cetane number are naphthalenes, naphtho-
cycloparaffins and triaromatics such as phenanthrene and
anthracene. Due to their lower resonance energies per
ring they are easily hydrogenated to the corresponding
hydroaromatic species. In saturating mixtures of poly-
nuclear aromatic compounds of varying degrees of ring
condensation, it may be shown by experiment that conver-
sion proceeds by successive hydrogenation of the poly-
nuclear aromatic rings[4]. For example, tables of cetane
numbers indicate that, in the hydrogenation sequence
naphthalene → tetralin → decalin, the greatest increase in
cetane value is achieved in the final step[5]. Generally,
for polynuclear aromatic species we expect the greatest
cetane improvement to occur when the final aromatic ring
is eliminated. Since in linearly annulated compounds the
final ring is more resistant to saturation, higher
processing severities are required for their complete
elimination.

aromatics (% M_a) (determined on a molecular basis by
mass spectrometry) versus cetane number. It is interest-
ing to compare this with the corresponding plot for per
cent aromatic carbon given in Figure 2. Figure 3 appears
to be almost linear except for some curvature in the high
cetane number area and it is apparent that we do not

obtain the same degree of curvature found in Figure 2.
The explanation for this phenomenon is that, when dealing
with aromatic molecular species rather than aromatic
carbons, we observe the effects of conversion of poly-
nuclear aromatic compound types to their corresponding
hydroaromatic forms during primary ring saturation. Thus,
at low severities, conversion of one aromatic hydrocarbon
group type to another maintains the overall total molecu-
lar aromatic content. For example, in this particular
case, the synthetic crude A distillate contains naphtha-
lenes, naphthocycloparaffins and fluorenes totalling
approximately 14% and these may all be converted to
corresponding hydroaromatic group types. The true curva-
ture of Figure 3 is better demonstrated by plotting the
major aromatic hydrocarbon group types in the feed and
products individually against cetane number. Table 2
shows that the predominant aromatic species are alkyl-
benzenes, benzocycloparaffins and benzodicycloparaffins.)
Figure 4 presents a plot of mass per cent versus cetane
number for these species and shows that the curves
approach zero values at different points. Again, recent
work showed that at the optimum operating conditions the
relative rates of hydrogenation of these species over
sulphided $Ni-W/\gamma-Al_2O_3$ are alkylbenzenes $>$ benzocyclo-
paraffins $>$ benzodicycloparaffins therefore relationships
in Figure 4 should be linked to these findings[6]. As
noted above, at the optimum conditions, we observe that

the conversion of alkylbenzenes is complete, but small
amounts of the other two monoaromatic species continue to
influence the cetane number beyond the value of 41. Thus
residual amounts of these components remain even after
severe processing. Figures 2 and 3 have some practical
significance in that they predict the extent of conversion
of aromatics hence the severity of processing required to
produce diesel fuel of a specific ignition quality from a
particular feedstock. Previous work also demonstrated
that such interrelations are complicated when extensive
cracking of hydrocarbons occurs[1].

In an earlier report, the impact of excessive concen-
trations of aromatics on jet fuel quality was discussed[7].
A standard procedure to measure the effect of aromatic
hydrocarbon concentrations on combustion quality may be
obtained from the smoke point test (ASTM D1322). Figure 5
presents plots of per cent aromatic carbon versus smoke
point (mm) for distillate products from secondary hydro-
treating of the feedstocks from syncrudes A and B. The
data for B are taken from a previous report[1]. As
expected, the quality of distillate from B is superior but
both fuels exceed the specification point of 20 mm which
is indicated in the figure. The distillate boiling range
is also somewhat wider than the usual Jet A specification
and a narrower cut to a lower end-point will produce a
lower aromatic content.

Correlation of hydrogen consumption with cetane number improvement

The hydrogen consumption during distillate upgrading may be an important factor in determining the economic feasibility of a particular process. Where hydrogen is in ample supply, e.g., from refinery reforming operations or from surplus natural gas, the question of hydrogen consumption may be less critical. Input of hydrogen to synthetic crude distillates for their improvement to specification grade fuels may also be viewed as a means of converting hydrogen to liquid fuels. An increased liquid yield achieved during aromatics saturation results from hydrogen addition.

In hydrotreating experiments the determination of mass balances is often difficult because of problems in eliminating experimental errors mainly associated with the determination of hydrogen pressures and gas flows[8]. We have found that the determination of the hydrogen consumption of a feed during processing using low resolution mass spectrometry is less problematical and gives reliable results.

The method is outlined as follows. The hydrogen content of a hydrocarbon is approximated by the number of hydrogen atoms divided by its molecular weight. Thus, the

hydrogen content of any molecule C_nH_{2n+z} is given by:

$$f_H = \frac{2n + z}{12n + 2n + z} \qquad (1)$$

where: f_H = the fraction by weight of hydrogen in the molecule: and z = the hydrogen deficiency. (The z number also classifies individual compounds into distinct hydrocarbon group types).

The hydrogen consumption for a chemical reaction is the difference in total hydrogen content between the product and feed. For any hydrocarbon group type, g_i, the hydrogen consumed during reaction, q_i, is related directly to the z number by:

$$q_i = \Delta Wg_i \cdot \frac{(2n + z_i)}{(14n + z_i)} \qquad (2)$$

where: ΔWg_i = the change in weight per cent of group type, g_i, in the total hydrocarbon mixture. The total amount of hydrogen consumed, Q, measured as dm^3 (hydrogen) dm^{-3} (feedstock) is then given by:

$$Q = 118.1 \cdot \rho \cdot \sum^i \Delta Wg_i \cdot \frac{(2n + z_i)}{(14n + z_i)} \qquad (3)$$

where: ρ is the specific gravity of the feedstock and 118.1 is the conversion factor from mass of hydrogen to gas volume. In this case $14n + z$ is the molecular weight and n the number of carbon atoms of the group type.

The average molecular weight of the group types may be estimated by considering that, in complex petroleum mixtures, the more hydrogen deficient molecules will have lower average carbon numbers than the more saturated types within a particular boiling range. Table 3 presents collated results showing carbon number equivalents of hydrocarbon types which were derived from the physical properties of a variety of hydrocarbons given in API projects[9,10]. The carbon number, P, of the paraffins is shown in the left hand column and the equivalent group type carbon numbers are shown in the rows. Table 3 also identifies z numbers for the different hydrocarbon group types.

The average carbon number of the paraffins may be obtained from the intensities of the de-isotoped sensitivity corrected distribution of the molecular ions of the paraffins series in the spectrum. Alternatively, the paraffinic average carbon number could be provided by simulated distillation data using gas chromatography.

Equation (3) is valid for those reactions where the yield of the hydrogenated product is 100% and cracking to lighter products such as naphtha does not occur. Where cracking to lighter products occurs, equation (3) must be modified to include their yields and hydrogen contents.

An examination of the relations between fuel ignition quality and chemical composition reveals that cetane

number may be related to hydrocarbon group type within fairly broad classifications[5],[7]. A progression of cetane improvement with changing chemical structure is discernible when comparing different hydrocarbon group types, e.g., 2-ring with single-ring aromatics or naphthenes with paraffins. However, a simplified picture of a cetane number scale is complicated by chain branching which produces poorer ignition quality and there is considerable overlap between groups[5].

The process of distillate refining under consideration here involves mainly the conversion of aromatic compounds to their corresponding naphthenes. Within the temperature range 300-380°C we expect little cracking of hydrocarbons and this is confirmed by Figure 9, the details of which are discussed below. We therefore expect an ordered input of hydrogen corresponding to a systematic conversion from one type of cetane rated component to another. From this it follows that we should be able to correlate the hydrogen consumed during aromatic saturation with the degree of cetane improvement.

Figure 6 presents a plot of hydrogen consumption versus the measured cetane number improvement. Values of Δ cetane number were obtained from the difference of values between product and feed as determined by engine test.

The plot is a smooth curve which intercepts the ordinate at approximately 25 dm^3 (hydrogen) dm^{-3} (feedstock). The apparent deviation of the intercept point from zero suggests that the input of low hydrogen levels into the feedstock has no impact on cetane number. Such low conversions are achieved under mild processing conditions and our interpretation of this phenomenon is that we observe the partial saturation of compounds such as naphthalenes and naphthocycloparaffins to their corresponding hydroaromatic forms. It is expected that these conversions will affect only marginally the cetane rating.

For the syncrude A distillate figure 6 shows that to raise the cetane number to the specification level of 40, i.e., by 9 points, an input of approximately 120 dm^3 (hydrogen) dm^{-3} (feedstock) (670 scf bbl^{-1}) is required. This value is somewhat lower than that found in other studies[11, 12], and may be attributed to differences in the feedstock cuts.

Alternative processes for upgrading middle distillates

The experimental results of this and previous investigations demonstrate that conversion of aromatics to naphthenes is a convenient hydroprocessing route for upgrading middle distillates of low hydrogen content.

However, important questions arise regarding the nature of the products generated and whether such distillates are acceptable for use as jet and diesel fuels. Table 2 indicates that after hydroprocessing at the optimum operating conditions the product consists of approximately 20 % paraffins, 79 % naphthenes and a residual amount of aromatics. It also shows that the naphthenic portion consists of approximately 39 % non-condensed monocyclo-paraffins, 28 % condensed dicycloparaffins and 12 % condensed polycycloparaffins. In the original feedstock the corresponding amounts were 21, 14 and 8 %respectively.

The high levels of condensed cycloparaffins in synthetic fuels raise questions regarding their fate in the combustion processes associated with jet and diesel applications. Possibly, under certain conditions, dehydrogenation reactions may revert polycyclic compounds back to their hydroaromatic forms and, by a process of further hydrogen loss, eventually form aromatics and then particulates. While single-ring compounds are expected to resist conversion, hydrogen abstraction is likely to occur in condensed cycloparaffins due to their abundance of weaker tertiary C-H bonds[12].

Apart from the health hazards associated with the formation of excessive amounts of particulates in diesel exhaust emissions, it is also well known that soot

particles generated in aviation turbines can cause severe maintenance problems[7]. Consequently new directions in catalytic refining of synthetic middle distillates may be required to eliminate excessive concentrations of polycyclic compounds. This would include the conversion of tetralins and decalins which are common ring compounds found in synthetic fuels.

For some time ring-opening reactions have been considered as a means of producing paraffins from naphthenes. Although much work has been carried out to investigate catalytic hydrocracking of hydrocarbons as a means of conversion to compounds of lower molecular weight, the selectivity required to produce suitable paraffinic compound types by ring-scission poses a new problem. In general, catalytic hydrocracking on suitable acidic supports such as silica-alumina produces branched hydrocarbons. This phenomenon is well known in catalytic cracking. An additional factor in hydrocracking which enhances the production of isoparaffins is the rapid saturation of branched olefinic species which might otherwise undergo readsorption and isomerize towards equilibrium[13]. Because of their more highly branched original structures, cycloparaffins yield even larger quantities of branched products than normal paraffins.

Work carried out thus far has demonstrated some of the effects of cracking of saturated ring compounds in synthetic middle distillates. In recent experiments, using a sulphided Ni-W/γ-Al$_2$O$_3$ catalyst at severe operating conditions, i.e., 400-440°C and 17.3 MPa the products generated were analyzed using low resolution mass spectrometry. The order of cracking reactivity in cycloparaffinic structures was related to the degree of ring-condensation. Thus, considering the cycloparaffins listed in Table 2, the ease of cracking was found to be 3-ring > 2-ring > single-ring. Effects ranged from centre-ring cracking in polycyclic structures to minimal ring-scission in less reactive monocyclic compounds[6]. These results suggest the possibility of ring-opening in condensed naphthenes with the generation of stable monocyclics.

Brunn and Lopez[14] patented a catalyst by which means polynuclear condensed aromatics are converted to condensed naphthenes by hydroprocessing over sulphided fluoride-promoted nickel-tungsten on silica-alumina. They claim that the initial reaction is followed by selective cracking of the condensed naphthenes to form alkyl naphthenes. They also suggest that the alkyl side chains formed by ring-opening are not severed. Although we consider this to be a desirable objective, experimental

results obtained so far indicate a different trend. Over sulphided Ni-W/γ-Al$_2$O$_3$ catalyst, on a typical acidic catalyst support, ring-opening of condensed naphthenes without substantial de-alkylation to lower boiling products was found to be unlikely. Addition of fluoride ions to Co-Mo/γ-Al$_2$O$_3$ catalysts was found to alter their hydrocracking activity in general, without causing significant changes in selectivity[15]. We believe that the changes observed are related to the surface acidity of supports. It is doubtful that an increase in surface acidity would favour ring-opening of condensed naphthenes without substantial de-alkylation to lower boiling products.

Figure 7 presents GC/MS results obtained for middle distillate from synthetic crude A. The total ion chromatogram shows the distribution of hydrocarbons over the complete boiling range. The figure indicates the normal paraffins from C$_{10}$ to C$_{18}$, which are typical of conventional jet and diesel fuels, as well as peaks identifying other hydrocarbon types by z number. Figure 8 shows a corresponding total ion chromatogram for product obtained after hydroprocessing at 440°C, LHSV 0.75 and 17.3 MPa. The latter results indicate that considerable cracking into the lower boiling range occurs with the generation of hydrocarbons typical of naphtha. While the

normal paraffins show reasonable stability under these
conditions, the results suggest cracking of ring compounds
to lower boiling products, which agrees with our previous
work. Considerable increases in concentrations of pentane
and methyl cyclohexane are indicated and it is most likely
that these species are the end products of ring-opening
and de-alkylation reactions. As noted above, we have
demonstrated in recent work that monocycloparaffins are
quite resistant to cracking under these processing condi-
tions[6]. For single-ring species, if large paraffinic
side-chains are present, they are also liable to crack
faster than the ring, producing lighter naphthenes and
aromatics[15]. In the present case, the cracking
reactions are likely to involve cleavage of two- and
three-ring naphthenes and severing of paraffinic side-
chains from cyclic compounds. Naturally, at the tempera-
tures used considerable dehydrogenation of naphthenes to
aromatics is also expected to occur[1].

The low resolution, non-separative mass spectrometric
method used in this work is also able to monitor the con-
centration of paraffins in the feed and products[3].
Figure 9 presents plots of mass per cent paraffins versus
operating temperature over the entire range, and at LHSV
0.75 and 2.00 h^{-1}. The horizontal broken line in the
figure indicates the initial amount of paraffins in the
feed.

The plots reveal the extent of cracking and it is apparent that small amounts of paraffins are produced at even the lowest temperatures. At the severest operating conditions (440°C, LHSV 0.75, 17.3 MPa) the paraffin concentration in the total product increased by approximately 7 %. Although this particular analytical method is not able to identify the type of paraffins produced nor their origin, it is most likely that the species generated will be iso-paraffins boiling in the low temperature range and, therefore, typical of naphtha products.

SUMMARY

The diesel ignition properties of the fuels were strongly related to the concentrations of aromatics as measured by two analytical techniques. In the case of aromatic carbon content, comparisons were made with previous results obtained for distillate from a synthetic crude produced by delayed coking of bitumen. These relationships indicate that certain aromatic compounds may significantly retrograde the cetane rating of synthetic fuels even when present in small amounts, but more work would have to be done to confirm this. Interrelations of jet fuel combustion quality with aromatic carbon content were also compared for distillates from syncrudes A and B. A method was described and used for the determination of hydrogen consumption of the feedstock during hydro-treatment and the degree of cetane improvement of distillate from syncrude A was correlated with the amount of hydrogen consumed.

GC/MS analyses revealed some of the effects of cracking in synthetic middle distillate under severe operating conditions. The results are in agreement with those we obtained recently using low-resolution non-separative mass spectrometry[6]. While monocyclic naphthenes are reasonably resistant to cracking, two- and three-ring species undergo cleavage more readily.

Although we consider hydrocracking of condensed naphthenes
with minimum de-alkylation to be a desirable process, it
is unlikely to be achieved with any success using existing
acidic catalyst supports because they do not seem to offer
good selectivity.

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FIGURE CAPTIONS

1. Summarized chemical changes during hydrotreating of middle distillates from Athabasca syncrudes.

2. Per cent aromatic carbon (^{13}C NMR) vs. cetane number for hydrotreated distillates from synthetic crudes A and B.

3. Mass per cent total aromatics vs. cetane number for hydrotreated distillate from synthetic crude A.

4. Mass per cent of monoaromatic species vs. cetane number for hydrotreated distillate from synthetic crude A.

5. Per cent aromatic carbon (^{13}C n.m.r.) vs. smoke point for hydrotreated distillates from synthetic crudes A and B.

6. Correlation of hydrogen consumption with cetane number improvement for hydrotreating distillate from synthetic crude A.

7. GC/MS spectrum for middle distillate from synthetic crude A.

8. GC/MS spectrum for hydrotreated middle distillate from synthetic crude A, 440°C, LHSV 0.75, 17.3 MPa.

9. Effect of temperature on formation of paraffins in distillate from synthetic crude A, 17.3 MPa.

TABLE 1

Properties of middle distillate feedstocks from Athabasca
synthetic crudes

	Synthetic Crude A (fluid coked bitumen)	Synthetic Crude B (delayed coked bitumen)
Relative density (15/15°C)	0.862	0.863
Carbon (wt%)	87.2	87.5
Hydrogen (wt%)	11.7	12.5
Sulphur (ppm)	97	550
Nitrogen (ppm)	37	54
Average molecular weight	200	201
% Aromatic carbon by ^{13}C n.m.r.	17.5	14.3
Cetane number (CCR method)	31	36
Distillation (D86)		
Initial b.p. °C	163	142
5%	183	
10%	192	181
20%	210	
50%	251	232
90%	296	283
Final b.p.	318	333

TABLE 2

Examples of fuel product compositions from synthetic crude A

before and after secondary hydrotreating

	Feedstock	Processing conditions and products			
		1	2	3	4
	Middle distillate from synthetic crude A	300°C LHSV 0.75 3.55 MPa	300°C LHSV 0.75 7.00 MPa	380°C LHSV 0.75 17.3 MPa	420°C LHSV 0.75 17.3 MPa
Paraffins	15.8	18.3	17.8	19.5	21.0
Total cycloparaffins	42.4	45.5	57.3	79.3	75.5
Non-condensed monocycloparaffins	20.5	22.5	26.4	39.2	38.3
Condensed dicycloparaffins	14.4	16.3	21.3	28.3	25.1
Condensed polycycloparaffins	7.5	6.7	9.5	11.8	9.1
Total aromatics	41.9	36.3	24.9	1.3	6.2
Alkylbenzenes	17.3	17.8	11.4	–	1.7
Benzocycloparaffins	12.9	13.4	9.4	0.5	3.1
Benzodicycloparaffins	5.2	3.6	2.9	0.6	1.4
Naphthalenes	3.5	1.0	0.6	0.2	0.3
Naphthocycloparaffins	1.6	0.1	–	–	–
Fluorenes	1.0	0.4	0.5	–	–
Triaromatics	0.4	–	–	–	–
% Aromatic carbon (^{13}C n.m.r.)	17.5	14.5	9.0	0.8	3.2
Cetane number (CCR method)	31	32.4	35.2	42.5	38.6

TABLE 3

Carbon number equivalents of hydrocarbon types

	Paraffins	Monocyclo-paraffins	Dicyclo-paraffins	Tricyclo + paraffins	Mono-aromatics	Di-aromatics	Triaromatics +	Aromatic sulphur
z number	2	0	-2	-4	-6,-8,-10	-12,-14,-16	-18	
10		P	P	P	P-1	P-3	-	P-4
11		↓	↓	↓	↓	↓	-	↓
12							-	
13							P-3	
14							↓	
15			↓	↓				
16			P-1	P-1	↓			
17			↓	↓	P-2			
18					↓		↓	
19							P-4	
20		↓	↓	↓	↓	↓	↓	↓

FIG. 1

Monoaromatic reduction to saturates
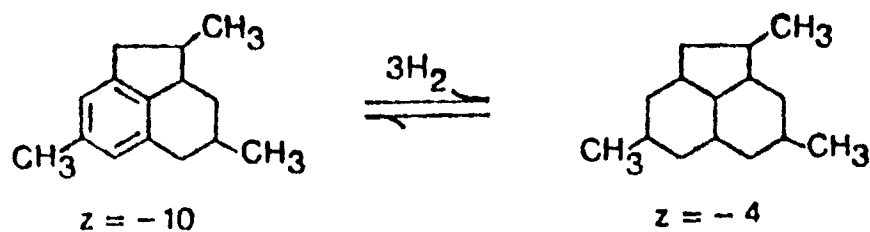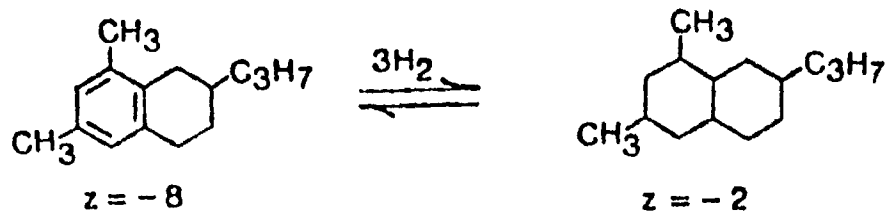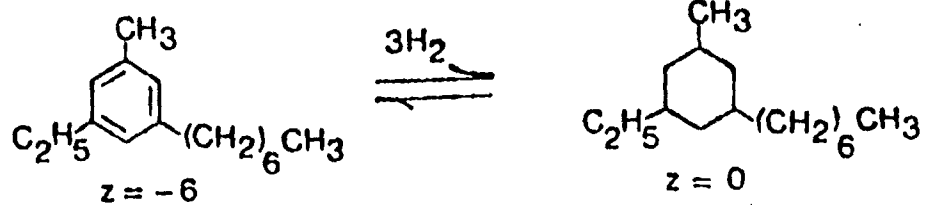
Diaromatic reduction

FIG. 2

FIG. 3

Mass % vs Cetane Number

Legend:
● Alkylbenzenes
△ Benzocycloparaffins
○ Benzodicycloparaffins

FIG. 5

FIG. 7

FIG. 8

FIG. 9