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IMPACT OF EXCESSIVE AROMATICS IN OIL SAND SYNCRUDES ON PRODUCTION AND QUALITY OF MIDDLE DISTILLATE FUELS

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IMPACT OF EXCESSIVE AROMATICS IN OIL SAND SYNCRUDES ON
PRODUCTION AND QUALITY OF MIDDLE DISTILLATE FUELS

by

M.F. Wilson*

ABSTRACT

Increased production from oil sands and heavy crude deposits is expected in Canada during the next two decades. Current processes for upgrading Athabasca bitumen produce synthetic crudes of such high aromatics content that diesel and jet fuels produced from oil sand distillates do not meet current specifications. It is expected that the increasing demand for these fuels will exert pressure on existing refineries and some relaxation of specifications in Canada is anticipated. Doubts also exist regarding the "burnability" of heating fuels from synthetic crudes. Some progress is expected in future upgrading methods and in downstream refining. However, research and development in new process technologies will be required in order to solve these problems.

*Research Scientist, Hydrocarbon Processing Research Laboratory, CANMET, Energy, Mines and Resources Canada, Ottawa.

L'IMPACT DE LA PRESENCE DE QUANTITES EXCESSIVES DE
COMPOSES AROMATIQUES DANS LE BRUT SYNTHETIQUE DU
SABLE PETROLIFERE SUR LA PRODUCTION ET LA QUALITE DES
CARBURANTS INTERMEDIAIRES DISTILLES

par

M.F. Wilson*

SOMMAIRE

Au cours des prochains 20 ans, on prévoit au Canada une augmentation de la production d'énergie à partir des sables pétrolifères et des gisements de brut lourd. Pour le moment, les techniques employées pour enrichir le bitume d'Athabasca donnent des bruts synthétiques ayant une teneur aromatique tellement élevée que les combustibles diesel et les carburateurs obtenus à partir des produits de distillation des sables pétrolifères ne rencontrent pas les normes actuelles. On s'attend à ce que l'accroissement de la demande de ces carburants exerce une pression sur les raffineries existantes et un assouplissement des normes au Canada est anticipé. Il existe aussi des doutes concernant les propriétés de combustion des combustibles provenant des bruts synthétiques. Le perfectionnement des méthodes d'enrichissement et du raffinage en aval est prévu pour l'avenir. Cependant, des travaux de recherche et de développement devront être entrepris afin de résoudre les problèmes.

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INTRODUCTION

As Canada moves towards energy self-sufficiency it is expected that in the 1980's an increasing proportion of the total crude oil supply will be synthetic crude from oil sands and heavy oil deposits in northern Alberta. The largest of these are located in the regions of Athabasca, Cold Lake and Peace River.

At present, synthetic crude oil is produced from two commercial operations which process bitumen from oil sands at Fort McMurray, Alberta. Suncor Inc., when fully operational, produces 9200 m³/d (58 000 barrels/day) and the larger Syncrude project 17 500 m³/d (110 000 barrels/day). This combined output is approximately 10% of the present total Canadian crude oil production. With projected expansions it is predicted that a total combined output of 41 300 m³/d (260 000 barrels/day) is possible from these operations (1). Other possible developments in synthetic crude oil production are the Cold Lake and Alsands projects which have been designed to produce 22 300 m³/d (140 000 barrels/day) and 21 800 m³/d (137 000 barrels/day), respectively.

Bitumen upgrading is achieved in the existing operations by coking processes. The polycyclic aromatic ring structures of the material are cracked to a lighter product which is then fractionated into coker distillates and upgraded further by severe hydrotreating which removes sulphur and nitrogen and also saturates olefins and some aromatics. The distillate streams are then blended to produce a synthetic crude oil.

Figure 1 presents boiling point ranges for various petroleum fuel products. The middle distillate fraction, covering approximately 140-350°C, includes diesel and jet transportation fuels and light and heavy fuel oils. The upgrading of Athabasca bitumen produces a synthetic crude with a middle distillate fraction containing a high concentration of aromatics. A high aromatics content is undesirable in both jet and diesel fuels, therefore synthetic crude is a poor feedstock for these products.

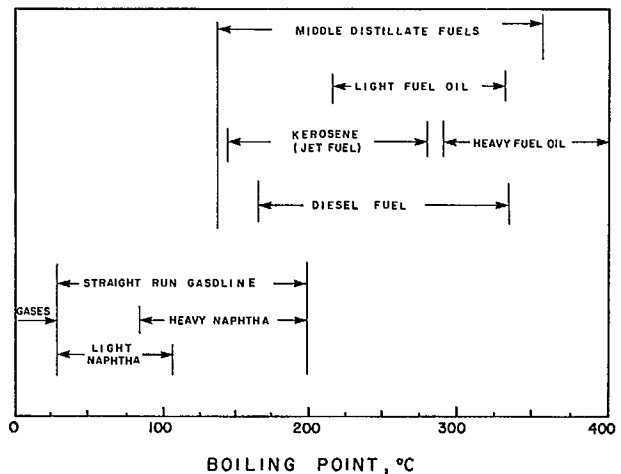


Fig. 1 - Boiling point ranges for fuel products

Figure 2 presents a forecast of Canadian gasoline and distillate fuel demand trends for the next two decades. Although motor gasoline consumption is expected to decline, the overall demand for transportation fuels is projected to increase steadily. At present the diesel fuel share of the Canadian crude oil barrel is 8% and is expected to increase to 14% by the end of the century. During this period the demand for jet fuel is also expected to double from the current level of 4% of the barrel to a substantial 8% (3). Figure 2 also indicates that the demand for heating fuel oil is projected to continually decline.

From the foregoing it is apparent that an increasing supply of highly aromatic synthetic crude oil from the Alberta oil sands together with a growing Canadian demand for middle distillate transportation fuels will exert considerable pressure on existing petroleum refining operations and threaten the quality of future fuel products. This report examines the consequences of these developments and discusses possible solutions.

CHARACTERISTICS OF DISTILLATE STREAMS

A comparison of some properties of a Canadian synthetic crude with conventional crude has been made by Steere et al and is shown in Table 1 (4). Synthetic crude is seen to have a

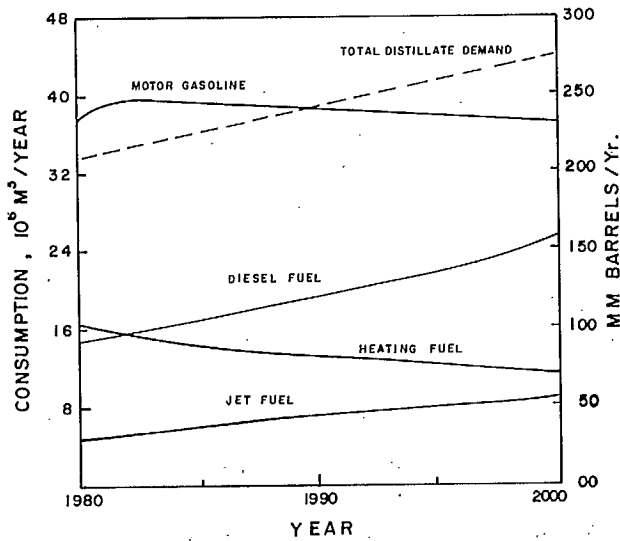


Fig. 2 - Forecast of Canadian gasoline and distillate fuel demand trends

Source: Reference 2

higher density and this results from its high aromatics content. The sulphur content is much lower than that of conventional crude because of the severe hydrotreating during upgrading. The pour point of the synthetic crude is very low because of its high alkylbenzene and relatively low waxy paraffin content. (Low pour and cloud points in middle distillates are good qualities for winter diesel fuels).

Table 1 shows that the naphtha content of the synthetic material is quite low at 18% compared with conventional crude at 36%. The naphtha is also found to have a high paraffin and low aromatics content making it a poor reformer feedstock for gasoline production (4). On the other hand the middle distillate fraction boiling between 195-345°C is seen to be very large at 47% compared with that of conventional crude at 31%. Since the demand for middle distillate fuels is

Table 1 - Properties of synthetic and conventional crudes

	Synthetic crude*	Conventional crude†
Gravity, °API	32	41
Density, kg/DM ³	0.865	0.820
Viscosity, cSt at 40°C	3.0	2.9
Sulphur, mass %	0.08	0.2
Nitrogen, mass %	0.03	0.04
Hydrogen, mass %	12.6	13.6
Pour point, °C	-45	-6
Distillate yield, LV %		
I - C ₅	4	3
C ₅ - 195°C	18	36
195 - 345°C	47	31
345 - 560°C	31	18
560°C +	0	12

* Syncrude Ltd.

† Canadian Federated Pipeline

Source: Reference 4

increasing this might have been an attractive feature, however, the high aromatics content presents a difficult problem for refineries. This is discussed fully in the following sections on diesel and jet fuels.

A structural analysis of synthetic distillates has been reported by Steere and Nunn (2). Mass spectrographic data for middle distillates from various sources are compared in Table 2 for synthetic distillate, straight run material and cracked gas-oil.

Synthetic distillate is seen to contain a significantly higher proportion of aromatics than conventional distillate but it is worth noting that the increased aromatic content is due to the increase in alkylbenzenes whereas in the cracked gas-oil there is a marked increase in 2-ring aromatics. Synthetic distillate also has a high amount of naphthenes but its paraffin content is only half that of conventional distillate, which accounts for the low cloud and pour points of synthetic fuels. An important distinction has also been made between the alkylbenzene types in synthetic and conventional distillates by using carbon-13 and proton NMR analysis (2). Results suggest that the single aromatic rings in synthetic material are much more alkylated than those in conventional distillates. This would confirm existing theories regarding the upgrading of oil sands bitumen whereby polycyclic aromatic structures are broken down in the coking process to simpler aromatic types. Table 1 also shows that the vacuum gas-oil fraction of synthetic crude is 31% of the total; this material can be used as a heavy fuel oil or cat-cracker feedstock.

Another important feature of synthetic crude is the absence of residual material, a significant factor in the design of the new Scotford refinery which will process no conventional crudes. A conventional refinery includes costly operations for handling and processing residuals. A 100% input of "bottomless" crude to the Scotford refinery will therefore be an important economic advantage.

DIESEL FUEL FROM OIL SAND DISTILLATES

OVERVIEW

General agreement exists throughout the petroleum industry that a critical situation is developing for diesel fuel production in Canada. Although the input of synthetic crude from oil sands operations creates a unique situation, it is worth noting that this is only part of the diesel fuel problem. To some extent a critical situation is developing world-wide mainly because of an increased demand for diesel fuel and a reduced demand for heating oil which releases poor quality material into the diesel pool.

The main points concerning future trends in diesel fuel quality and supply in Canada are:

- (i) Of all petroleum fuel products diesel fuel is showing the most rapid growth, and this is expected to continue at approximately 4%/a into the 1990's.
- (ii) Considerable pressure will be exerted on Canadian refineries to satisfy a growing demand while attempting to maintain diesel fuel quality.

Table 2 - Compositional analysis of middle distillates by mass spectrograph

Mass %	Synthetic distillate	Conventional distillate	Cracked gas-oil
Paraffins	17	39	19
Naphthenes	37	34	16
Alkylbenzenes	36	18	34
2-ring aromatics	8	8	28
3-ring aromatics	2	1	3

Source: Reference 2

- (iii) It is predicted that diesel fuel ignition quality will deteriorate during the 1980's.
- (iv) Two major factors will affect diesel fuel ignition quality in Canada:
 - (a) A declining demand for heating fuel which will release more cracked gas-oil of low cetane number into the diesel pool.
 - (b) The increasing production from oil sands of synthetic fuels which have a high aromatics content.
- (v) The decline in diesel fuel ignition quality will be counteracted to some extent by increased use of diesel ignition improver additives.

Many Canadian refineries are now processing synthetic crude oil; current practice is to blend the material with conventional crudes to produce a middle distillate with a lower aromatics content. As a result diesel fuel requirements may restrict the amount of synthetic crude which can be processed through the refinery. Since it is expected that in the future diesel fuel suppliers will be blending close to the specification limits it is generally agreed that an extensive review of the procedures for evaluating the cetane index of fuel streams is required.

DIESEL FUEL IGNITION QUALITY, CETANE NUMBER AND CETANE INDEX

The cetane number of a diesel fuel is a measure of ignition quality and is a numerical value obtained by carrying out a comparative test using a standard Cooperative Fuels Research (CFR) test engine. This device measures the delay period between fuel injection and ignition for a blend of reference fuels and also for the fuel under test.

The reference fuels are n-cetane, which has excellent diesel ignition qualities, i.e., produces a short ignition delay period, and heptamethylnonane which has poor ignition qualities; they are blended to produce a fuel which has the same ignition delay period as the test fuel.

On a cetane number scale pure n-cetane is arbitrarily assigned 100 and heptamethylnonane 15. The cetane number of the fuel blend is therefore

a function of the percentage of n-cetane which is given by:

$$\text{Cetane No.} = \% \text{ n-cetane} + 0.15(\% \text{ heptamethylnonane}) \quad (5)$$

Higher cetane numbers are synonymous with short ignition delay periods and good fuel ignition quality.

Poor quality diesel fuel of low cetane number may give rise to a significant number of problems affecting engine performance and environmental considerations. Figure 3 summarizes such problems (6,7).

It is apparent that diesel fuel producers must exercise careful control of fuel ignition quality. Since the CFR engine test is a method which is impractical in everyday refinery operations the cetane index method was introduced. In the past the ASTM D976 calculated cetane index formula has been used widely to predict the cetane number of diesel fuels. The formula is based on two physical properties, i.e., API gravity and mid-boiling point.

The ASTM D976 formula is not applicable to synthetic fuels and some refiners have disre-

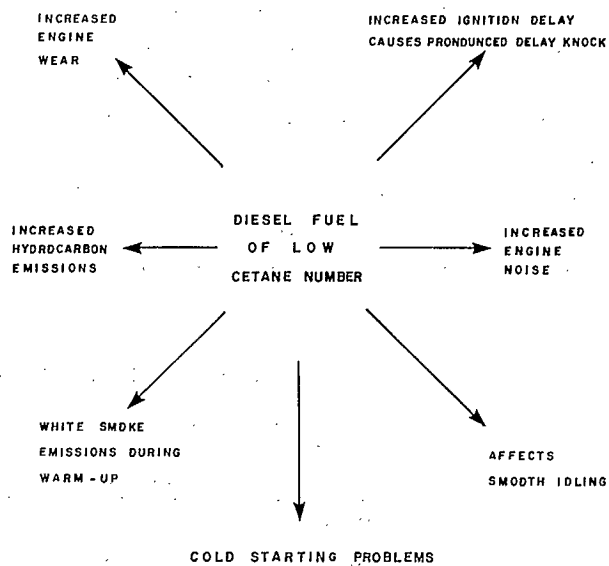


Fig. 3 - Diesel fuel ignition quality and engine performance

garded this proviso with unfavourable consequences. In some cases the cetane numbers of fuels containing synthetic distillates have been overestimated by up to 11 numbers (2). The formula is also not applicable to fuels containing cetane improver additives.

At present a task force of the Canadian Government Specifications Board (CGSB) is developing a new formula to predict the cetane numbers of fuels containing synthetic distillates. It is expected that the new cetane index formula will contain aniline point as one of the parameters.

One of the problems in developing a good quality diesel fuel from an unconventional crude oil source is understanding the relationship between chemical composition of a distillate and its ignition quality as measured by the cetane number. As more synthetic crude materials are considered for middle distillate production, a better understanding of such relationships may become necessary. Table 3 presents data for cetane numbers and boiling points of pure hydrocarbons. Some general comments follow concerning chemical structure and cetane number. Essentially, hydrocarbons with the most favourable cetane numbers are paraffins having long straight chains up to about C₂₀. Paraffins having branched chains are less favourable and as a rule the greater the degree of branching the lower the cetane number. Thus, heptamethylnonane has a cetane number of 15. Naphthenes generally have lower numbers than paraffins but they are not as low as those of the aromatics which have the lowest cetane values. Within the aromatics group it is seen that condensed ring compounds such as naphthalenes have the poorest ignition qualities. It should be noted that this is a simplified picture of the cetane number scale and there is considerable overlap between groups.

Appendix 1 presents details of a proposed new CGSB diesel fuel specification, CAN 2-3.6, which contains only three fuel types. Types AA and A relate to No. 1-D fuel requirements and are not intended for low-speed stationary engine applications. Type B, whose low temperature performance is determined by seasonal and local

requirements, is the only type relating to No. 2-D fuels.

In the proposed specification all grades have a minimum cetane number of 40 and it is also proposed that a calculated cetane index may be used for control purposes provided the buyer and seller agree on the approximate relationship between the calculated value and the cetane number as determined by the D613 method for fuel supplied.

CHARACTERISTICS OF DIESEL FUEL FROM SYNTHETIC CRUDE

It was noted previously, when considering the properties of synthetic crude, that the volume of the fraction boiling in the middle distillate range is very large, i.e., approximately 47%. Unfortunately, a significant proportion of the components of this material does not meet diesel ignition quality requirements.

A comparison of the properties of diesel fuels produced from both synthetic and conventional crude sources has been made by Steere et al (4). Table 4 summarizes characteristics of the two fuel types. Data show that a significantly higher level of aromatics is present in the synthetic fuel - 44% compared with that of conventional fuel - 32%. This difference is also reflected in the higher density of the synthetic product. As expected, the cetane number of the synthetic product is low, i.e., 34 compared with 48 for conventional fuel and the cetane value falls well below the CGSB specification minimum of 40. It is also interesting to compare the cetane index with cetane number for both fuels. It is apparent that the cetane number has been grossly over-predicted for the synthetic fuel, using the ASTM D976 cetane index.

The low cloud and pour points of synthetic diesel fuel shown in Table 4 may be regarded as one of its attractive features. The operation of diesel engines at low temperatures is sometimes affected by wax precipitation which may cause blockage of fuel filters and lines; this can be particularly problematical in the Canadian far north. The reduced wax content of

Table 3 - Cetane number and boiling point of pure hydrocarbons

Paraffins				Naphthenes			
Empirical formula	Hydrocarbon	Boiling point, °C	Cetane No.	Empirical formula	Hydrocarbon	Boiling point, °C	Cetane No.
(a) n-Paraffins							
C ₇ H ₁₆	n-Heptane	98.4	56	C ₆ H ₁₂	Cyclohexane	80.8	13
C ₁₀ H ₂₂	n-Decane	212.2	76	C ₇ H ₁₄	Methylcyclohexane	100.3	20
C ₁₂ H ₂₆	n-Dodecane	216.3	80	C ₁₂ H ₂₂	Bicyclohexyl	238.5	53
C ₁₃ H ₂₈	n-Tridecane	236.5	88	C ₁₂ H ₂₄	3-Cyclohexylhexane	87-89 ¹⁰ (220)	36
C ₁₄ H ₃₀	n-Tetradecane	253.5	93	C ₁₆ H ₃₂	2-Methyl-3-cyclohexyl-nonane	177-180 ⁵ (345)	70
C ₁₅ H ₃₂	n-Pentadecane	272.7	95	C ₁₉ H ₃₈	1-Methyl-3-dodecylcyclohexane	177-180 ⁵ (345)	70
C ₁₆ H ₃₄	n-Hexadecane (cetane)	286.5	100	C ₂₀ H ₄₀	2-Cyclohexyltetradecane	197-199 ²⁰⁰ (255)	57
C ₁₇ H ₃₆	n-Heptadecane	305.8	105	C ₂₂ H ₄₄	2-Methyl-2-cyclohexyl-pentadecane	195-198 ¹⁰ (350)	45
C ₁₈ H ₃₈	n-Octadecane	317.9	110	C ₂₅ H ₅₀	1,2,4-Trimethyl-5-hexadecylcyclohexane	204-205 ² (405)	42
C ₁₉ H ₄₀	n-Nonadecane	336.2	110	C ₂₆ H ₅₂	5-Cyclohexyleicosane	231-233 ⁴ (420)	66
C ₂₀ H ₄₂	n-Eicosane	205.0 ¹⁵ (345)	110	(a) Decalins			
(b) Branched chain paraffins				C ₁₀ H ₁₈	Decalin	185.5	48
C ₆ H ₁₄	2-Methylpentane	60	33	C ₁₃ H ₂₄	n-Propyldecalin	245-247 ⁷⁴³ (250)	35
C ₆ H ₁₄	3-Methylpentane	63.2	30	C ₁₄ H ₂₆	n-Butyldecalin	263.5-264.0	31
C ₈ H ₁₈	2,2,4-Trimethylpentane	99.3	12	C ₁₄ H ₂₆	sec-Butyldecalin	261.5-263.0 ⁷⁴¹ (263)	34
C ₁₂ H ₂₆	3-Ethyldecane	201.5-202.5	48	C ₁₄ H ₂₆	tert-Butyldecalin	263-264	24
C ₁₂ H ₂₆	4,5-Diethyloctane	192-194	20	C ₁₈ H ₃₄	n-Octyldecalin	325-327 ⁷⁴⁶ (327)	31
C ₁₂ H ₂₆	2,3,4,6,6-Pentamethylheptane	176 ⁷³⁷ (180)	9	C ₁₈ H ₃₄	4-Methyl-4-decalylheptane	138-139	21
C ₁₃ H ₂₈	2,5-Dimethylundecane	214-216	58	C ₂₀ H ₃₈	3-Methyl-3-decalylnonane	173-176 ⁶ (337)	18
C ₁₃ H ₂₈	4-Propyldecane	215	39	C ₂₁ H ₄₀	2-Methyl-2-decalyldecane	156-158	37
C ₁₃ H ₂₈	5-Butylnonane	213	53	(b) Tetralins			
C ₁₄ H ₃₀	2,7-Dimethyl-4,5-diethyloctane	117 ¹³ (245)	39	C ₁₃ H ₁₈	n-Propyltetralin	256-258	8
C ₁₆ H ₃₄	5-Butyldodecane		45	C ₁₄ H ₂₀	n-Butyltetralin	269-270	18
C ₁₆ H ₃₄	7,8-Dimethyltetradecane	268-270	40	C ₁₄ H ₂₀	sec-Butyltetralin	268-270	7
C ₁₇ H ₃₆	7-Butyltridecane	147 ¹² (280)	70	C ₁₄ H ₂₀	tert-Butyltetralin	265-267	17
C ₁₈ H ₃₈	9-Methylheptadecane	173 ¹⁰ (320)	66	C ₁₈ H ₂₈	n-Octyltetralin	324-326 ⁷⁴⁰	18
C ₁₈ H ₃₈	8-Propylpentadecane	206	48	C ₂₆ H ₄₄	di-n-Octyltetralin		26
C ₁₈ H ₃₈	7,8-Diethyltetradecane	139-141 ¹⁹ (260)	67	Aromatics			
C ₁₈ H ₃₈	5,6-Dibutyldecane	156-157	30	(a) Alkylbenzenes			
C ₂₀ H ₄₂	9,10-Dimethyloctadecane	138-152 ² (325)	59	C ₁₁ H ₁₆	n-Amylbenzene	204-205	8
C ₂₁ H ₄₄	7-Hexylpentadecane	183 ^{9.5} (335)	83	C ₁₂ H ₁₈	n-Hexylbenzene	226-227	26
C ₂₂ H ₄₆	2,9-Dimethyl-5,6-di-isoamyldecane	153-155	48	C ₁₃ H ₂₀	n-Heptylbenzene	240-241	35
C ₂₄ H ₅₀	9,10-Dipropyloctadecane	174-177 ¹¹² (380)	47	C ₁₄ H ₂₂	n-Octylbenzene	255.5-257.5	31
C ₂₄ H ₅₀	10,13-Dimethyldocosane		56	C ₁₄ H ₂₂	2-Phenyldecane	123-125 ²⁰ (240)	33
C ₂₄ H ₅₀	9-Heptylheptadecane	210 ⁸ (375)	87	C ₁₅ H ₂₄	n-Nonylbenzene	280-281	50
Olefins				C ₁₆ H ₂₆	n-Octylxylene		20
(a) Mono-olefins				C ₁₇ H ₂₈	2-Phenylundecane	142-146 ⁶ (297)	51
C ₁₄ H ₂₈	1-Tetradecene	124.5-125.0 ¹⁵ (250)	79	C ₁₈ H ₃₀	n-Dodecylbenzene	172-173 ⁹ (338)	68
C ₁₆ H ₃₂	1-Hexadecene	275	88	C ₁₈ H ₃₀	4-Phenyldecane	138-141 ³ (308)	42
C ₁₆ H ₃₂	5-Butyl-4-dodecene	265-267	45	C ₁₉ H ₃₂	7-Phenyltridecane	183-184 ²⁰ (312)	41
C ₁₆ H ₃₂	Tetraisobutylene	240 ⁷²⁸ (245)	42	C ₂₀ H ₃₄	n-Tetradecylbenzene	195-196 ⁹ (352)	72
C ₁₇ H ₃₄	7-Butyltridecene		36	C ₂₀ H ₃₄	2-Phenyltetradecane	185-188 ⁷ (348)	49
C ₁₈ H ₃₆	9-Methyl-9-heptadecene		66	C ₂₂ H ₃₈	2-Methyl-2-phenylpentadecane	193-195 ⁷ (358)	39
C ₁₈ H ₃₆	7,10-Dimethyl-8-hexadecene		43	C ₂₆ H ₄₈	5-Phenyleicosane	235-238 ⁵ (433)	39
C ₁₈ H ₃₆	8-Propyl-8-pentadecene	168 ⁸ (320)	45	(b) Naphthalenes			
C ₂₁ H ₄₂	7-Hexyl-7-pentadecene		47	C ₁₁ H ₁₀	α-Methylnaphthalene	245	0
C ₂₄ H ₄₈	10,13-Dimethyl-11-doeicosene		56	C ₁₄ H ₁₆	α-n-Butylnaphthalene	282.5-283.5	6
(b) Di-olefins				C ₁₄ H ₁₆	β-tert-Butylnaphthalene	272-275	3
C ₈ H ₁₆	Di-isobutylene	102.6	10				
C ₁₆ H ₃₀	2,6,7-Trimethyl-2-6-tridecadiene	115-117 ³ (275)	24				
C ₁₈ H ₃₄	3,12-Di-ethyl-3,11-tetradecadiene	171.5-172.0 ⁶ (330)	26				

Raised figures after the boiling point indicate the pressure in millimetres of mercury at which the boiling point was determined. A figure in brackets following the boiling point indicates the calculated boiling point at 760 mm Hg (101.325 kPa).

Table 4 - Properties of diesel fuel from synthetic and conventional crudes

	Synthetic	Conventional
Density, kg/DM ³	0.874	0.833
Viscosity, cSt at 40°C	3.3	2.9
Cloud point, °C	-27	-10
Pour point, °C	<-50	-18
Sulphur, mass %	0.03	0.30
Nitrogen, ppm	25	15
Aromatics, vol % (D1319)	44	32
Cetane No. (D613)	34	48
Cetane index (D976)	42	51
Distillation (D86)		
IBP °C	157	158
10%	192	226
50%	274	271
90%	329	311
FBP	334	320

Source: Reference 4

synthetic middle distillates therefore makes them most suitable for blending with high cetane conventional gas-oils for the production of low cloud winter products. Other positive features of synthetic diesel fuel are good stability during storage and a low sulphur content. These properties result from severe hydrotreating of the coker distillates. A high sulphur content is undesirable in diesel fuel since the sulphurous and sulphuric acids formed may cause excessive wear of piston rings and cylinders.

USE OF SYNTHETIC DIESEL FUEL IN CANADIAN LOCOMOTIVES

Diesel engine size, operating speed and load range are important factors in determining engine cetane number requirements. For example, certain large slow-speed engines running as low as 100 rpm may operate with heavy fuels of cetane number 20. The small high-speed diesel engines running at 1500 rpm and over, which are used in automobiles and trucks, require rapid combustion

and cetane numbers of at least 40 (5). Railway diesel engines run at intermediate speeds of about 1000 rpm and locomotive engine designers originally planned to use the readily available ASTM No. 2-D fuel with requirements set out in the ASTM D975 Specification. The cetane number minimum of this fuel is 40.

For many years CN and CP Rail have considered alternative fuel sources and have carefully evaluated fuels on the basis of availability, quality and relative price (8). In 1969, Great Canadian Oil Sands Ltd. (GCOS) began production of synthetic crude oil from Athabasca bitumen at Fort McMurray and the following year CP and CN Rail, in conjunction with the National Research Council, began tests on a potential railway diesel fuel from this synthetic crude source.

The original synthetic diesel fuel was produced by making a blend of GCOS (now Suncor Inc.) naphtha, kerosene and gas-oil streams. However, this fuel was found to give cloud point

problems and precipitated wax at about -30°C , blocking fuel filters (9). Today the fuel supplied by Suncor is produced from a gas-oil side stream (GOSS) which is a by-product of the gas-oil Unifiner, a hydrotreating unit installed primarily to remove sulphur (10). Although some saturation of hydrocarbons is achieved in the hydrotreating step the GOSS fuel has a high aromatics content and consequently the fuel produced has a cetane number typically about 35 (8).

Since the time this fuel was introduced into railroad operations, data from tests indicate favourable results and the Suncor GOSS diesel fuel is now used extensively throughout Western Canada by CN and CP Rail. The fuel probably accounts for up to 10% of the Suncor plant output and is approximately 10% of all fuel consumed by CN and CP Rail locomotives (8).

The GOSS railway diesel fuel properties meet most of the ASTM No. 2-D diesel specifications but as noted previously the minimum cetane number requirement is not met. The fuel has been used since 1974 and has shown no decrease in engine performance or increase in maintenance costs. Table 5 presents specifications data comparing the summer and winter grades of the synthetic diesel fuel with ASTM No. 2-D fuel (8). In general, the synthetic fuel has competitive properties, particularly for mass per cent of sulphur; the low level is an important factor in minimizing corrosion and engine wear. It should be noted that the specified cetane number minimum

of the Suncor railway diesel fuel is listed as reportable and is typically about 35 as mentioned above. Table 5 shows summer and winter grades of synthetic diesel fuels; however, with the general use of "hot well" fuel preheating units in the CN rail engines the winter grade will eventually be dropped (8).

In conclusion it may be stated that the use of a GOSS from an oil sands plant to produce an unblended railway diesel fuel is a unique example of matching a synthetic fuel to a market outlet. Developing other similar outlets for low cetane number diesel fuels may be a continuing trend in Canada.

PROPOSED SOLUTIONS TO THE DIESEL FUEL PROBLEM

At present there is no consensus among petroleum refiners on how the growing Canadian diesel fuel problem will be resolved. Presumably in the short term at least, a number of compromise solutions will evolve which will be determined by economic and market forces affecting the diesel fuel supply. The long term prospects for diesel fuel from synthetic crude oil are less clear.

Figure 4 summarizes proposed solutions to the diesel fuel supply problem in Canada and these are discussed below.

Blending of Synthetic with Conventional Crude

Blending is the current practice for accommodating synthetic crude in refinery operations and the amount blended is a function of the

Table 5 - Some specifications for railway locomotive diesel fuels

	ASTM	Oil sands fuel*	
	No. 2-D Fuel	Winter Grade C-30	Summer Grade C-0
Cetane No., min.	40	†	†
Viscosity, cSt at 40°C , min.	1.9	1.8	1.8
	max.	4.1	3.5
Distillation, 90%, max.	338°C	295°C	320°C
<u>Sulphur, mass %, max.</u>	0.5	0.2	0.2

*CN Rail Specification 390-1C, Sept. 1978.

† Reportable, typically about 35

Source: Reference 8

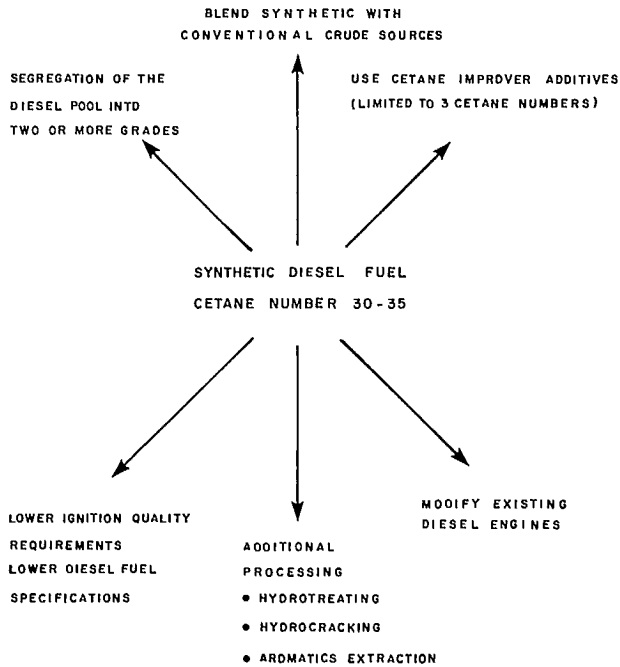


Fig. 4 - Proposed solutions to the diesel fuel supply problem in Canada

total product slate. Refineries are usually limited to a synthetic crude intake of between 20-30% and middle distillate fuels are usually the limiting factor. Apart from raising the aromatics content of middle distillates, blending of synthetic crude may also create other problems. Physical properties such as density, viscosity and flash point may be changed. Blending is possible provided there is a sufficient supply of conventional crude with good properties.

Use of Cetane Improver Additives

For some years diesel ignition improver additives have been used for raising the cetane numbers of distillate fuel stocks. It is claimed that they are effective in fuels regardless of the crude source and refining methods. In the past such additives have been used by refiners to release more low-cetane cat-cracked distillates into the diesel pool. It is anticipated that cetane improvers will continue to be used to enhance the ignition quality of diesel fuel from synthetic crude.

At present Ethyl Corporation sells DII-3 (Diesel Ignition Improver 3) which contains octylnitrate as the main constituent. Amylnitrate and hexylnitrate have also been used. The degree of cetane number improvement varies from fuel to fuel. In "typical" diesel fuels it is claimed that the addition of 0.1 V/V % of additive will provide an increase of between three to seven cetane numbers (11). It is generally believed that an improvement of up to three cetane numbers is possible at reasonable cost in diesel fuel containing distillates from synthetic crude. The use of cetane improver additives is therefore only a partial solution to the diesel supply problem in Canada and their general use is limited by economics.

Modification of Existing Diesel Engine Design

There is some scope for change in diesel engine design and several proposals for engine development have been made in recent years. The most significant of these are spark-assisted diesel engines, changes in fuel injection techniques to obtain "mechanical cetanes" and the use of diesel fuel preheaters in automobile and truck engines. (Preheaters would change some of the fuel flow properties such as density and viscosity. It is likely that seasonal adjustments to fuel preheaters would be required).

Many experts do not believe that a massive conversion to diesel powered automobiles will occur in Canada and in the next two decades it is predicted that the most significant areas of diesel fuel growth will be in light and medium trucks, industrial equipment and agricultural machinery. Put simply, this would amount to a future fuel distribution situation in which gasoline would be used predominantly in the private sector and diesel fuel in the commercial.

An important point of view expressed by some observers is that vehicle designers and manufacturers have in the past produced certain engine types and dictated the quality of fuel required to operate them efficiently and with a minimum of wear. In a situation where energy reserves must be conserved and maximized it is

now argued that fuel availability must determine engine design and in Canada a certain kind of diesel fuel will be produced in the future for which engines will have to be designed.

An important response to this point of view is that engine manufacturing in Canada is a branch plant economy and it is unlikely that world-wide vehicle suppliers will produce engines specifically for Canadian use. For example, it is predicted, that in the United States shale oils could satisfy a large proportion of future transportation fuel demand. These materials have a more favourable hydrogen/carbon ratio and synthetic fuels produced from these would have a significantly higher paraffin content than fuels from Athabasca bitumen.

At present some manufacturers of light trucks are experimenting with new engine designs. Test programs are also being carried out in Canada by government and industry to understand more about the performance of synthetic diesel fuels in conventional engines. It is hoped that these programs will result in changes in engine design.

Development of New Processes for Synthetic Diesel Fuel

This subject includes hydrotreating, hydrocracking, extraction of aromatics and alkylation. It is dealt with in the final section of this report.

Relaxation of Diesel Fuel Specifications

The proposed CGSB specification for diesel fuel presented in Appendix 1 shows that at present the cetane number minimum would be 40. Because of increasing demand it is predicted that there will be pressure from refiners to push the cetane number minimum lower. For example, it has been claimed that by lowering the cetane number minimum one point to 39 the total diesel pool could be increased by as much as 3% (2). Should this trend continue, it is conceivable that eventually two separate diesel fuel grades will emerge each with a distinct cetane number minimum.

Segregation of the Diesel Pool into Two or More Grades

Segregating the diesel pool into different grades has been suggested by Steere et al (4). The idea is to utilize the lowest cetane grade fuel to satisfy the needs of the low- and medium-speed diesel engine market. A fuel of the lowest grade could be used in industry or by railways and marine engines. The higher cetane grade fuels would be reserved for that part of the market which supplies automobiles and light trucks. It has also been proposed that trucks could be fitted with dual fuel tanks; a high ignition quality diesel fuel would be used for cold starting and a low quality fuel (cetane No. 35) could be used for cruising. This would push lower grade diesel fuel into the commercial sector. One might expect increased engine wear in this sector which would be offset by using cheaper fuel.

DIESEL FUEL EXHAUST FUMES AND CARCINOGENICITY

Recently Japanese cancer researchers claimed to have found evidence that diesel engine exhaust fumes may be responsible for increasing cases of lung cancer in Tokyo and other Japanese industrial areas. Diesel engines are widely used in Japan to power vehicles, electric generators and ships.

Increased hydrocarbon emissions from diesel engines can result from low ignition quality fuels which affect engine performance. One expert has commented that, with the increased use of oil sand derived fuels of high aromatic content, it is likely that this will result in increased carcinogenicity of the "soot" fraction in diesel exhaust from the use of these fuels (12).

JET FUEL FROM OIL SAND DISTILLATES

CANADIAN JET FUEL TYPES

The present civil jet fuel specifications used in Canada cover three types: Jet A-1 and

Jet A-2 fuels which are aviation kerosene types and differ only in flash and freezing point requirements (specification CAN 2-3.23, see Appendix 2) and Jet B fuel, an aviation wide-cut type (specification CAN 2-3.22). Wide-cut fuels consist of mixtures of naphtha and kerosene.

The Jet A-1 kerosene fuel is the standard grade used by international airlines and is a safer fuel with a 38°C flash-point. The Jet B fuel is also widely used in Canada (approximately 40% by volume of the total Canadian consumption in 1980) and is particularly suited to northern climates because of its lower freezing point and good cold starting properties (14). The terms Jet A-1 and Jet B have now achieved international usage to describe the basic kerosene and wide-cut types of civil jet fuel.

FUEL AROMATICS CONTENT AND JET TURBINE PERFORMANCE

The most important factors relating to jet fuel quality are those influencing energy content and combustion characteristics; such factors will determine the overall performance when the fuel is burned in a gas turbine. The chemical composition of a fuel, particularly the hydrogen/carbon ratio, is an important factor in determining both burning quality and energy efficiency. Thus, fuels which are hydrogen deficient such as those with a high aromatics content are more difficult to burn than mixtures which are richer in paraffins.

Fuels having a low H/C ratio also burn with more radiant flames which raise combustor liner temperatures and shorten engine life. High levels of aromatics in jet fuel also cause smoke formation under high power conditions and carbon deposits may form in the turbine causing damage when they become detached. Excessive aromatics can also degrade the elastomer components of fuel systems and may produce fuel mixtures with elevated freezing points. Thus, it is generally agreed that the burning of jet fuels which are hydrogen deficient will cause excessive wear on aircraft components resulting in increased maintenance costs.

The combustion performance of jet fuel is defined by one of three control tests included

in CGSB specification CAN 2-3.23. These are: measurement of luminometer number (ASTM D1740), smoke point test (ASTM D1322) or smoke point plus maximum naphthalenes content (ASTM D1840). The smoke point is the maximum flame height, in millimetres, at which a fuel can be burnt in a standard wick-fed lamp without producing smoke. At present the minimum smoke point is 20 mm. The aromatics content in these specifications is set at 22% maximum, mainly to control the elastomer compatibility aspects.

IMPLICATIONS OF PRODUCING JET FUEL FROM SYNTHETIC CRUDE

Properties of kerosene produced from synthetic crude are compared with those of conventional kerosene in Table 6 together with the corresponding Jet A-1 specifications. It is seen that synthetic kerosene has an aromatics content of 32% compared with 19% for conventional kerosene and the specification maximum of 22%. As expected, the smoke point and luminometer number of the synthetic fuel are also well outside the specification limits. On the other hand the naphthalenes content is significantly lower than that of conventional kerosene and this is because most of the 2-ring aromatics remain in the gas-oil fraction. The synthetic kerosene fraction is a relatively light portion of the middle distillates, boiling between 140-285°C. Chemical analysis by NMR and mass spectrograph has revealed that the aromatics content is predominantly of the single ring alkylbenzene type (2).

The cold temperature properties of synthetic kerosene are similar to those of synthetic diesel fuel. Since these fuels have a low paraffin content they have good cold flow characteristics and are free from the waxes which are contained in conventional kerosene.

FUTURE DEVELOPMENTS AND PROPOSED SOLUTIONS TO THE JET FUEL PROBLEM

The latest edition of CAN 2-3.23 contains the most recent relaxations in kerosene jet fuel specifications, i.e., the system of "reportable" fuels (Appendix 2). Note 5 of the specification states that fuel having an aromatics content of

Table 6 - Properties of kerosene from synthetic and conventional crudes

	Synthetic	Conventional	Jet A-1 Specifications
Density, kg/DM ³	0.830	0.803	0.839 max.
Viscosity, cSt at 40°C	1.3	1.2	-
Freeze point, °C	<-60	-50	-47 max.
Sulphur, ppm	38	100	2000 max.
Nitrogen, ppm	4	2	-
Hydrogen, mass %	12.9	13.9	-
(D3701)*			
Aromatics, LV %	32	19	22 max.†
(D1319)*			
Naphthalenes, mass %	0.6	2.2	3 max.
(D1840)*			
Smoke point	13	22	20 min.†
(D1322)*			
Luminometer no.	29.3	47.3	45 min.†
(D1740)*			

*ASTM test methods

† reportable to 25% vol max. aromatics
18-mm min. smoke point
40 min. luminometer no.

Source: Reference 4

more than 22% by volume, but not exceeding 25% is permitted provided the supplier notifies the purchaser or chairman of the Airport Fuel Handling Committee of the aromatics content within 30 days. Similar relaxations also apply to minimum smoke point and luminometer number. In attempting to establish jet fuel specification limits a complicating issue concerns the chemical composition of the aromatics in synthetic kerosene and the correlation with H/C ratio. As indicated above, the aromatic components are mainly of the alkylbenzene type.

Many experts claim that the hydrogen content of a fuel as measured by the NMR method (ASTM D3701) is one of the most reliable indicators of jet fuel combustion quality in terms of flame radiation effects and increased combustor liner temperatures (13). On the other hand it is argued that the aromatics content of a fuel as measured by the FIA test (ASTM D1319) is a relatively poor predictor of adverse flame radiation

effects (14). (The FIA method is a general test for hydrocarbon types and determines saturates, non-aromatic olefins and aromatics using a fluorescent adsorption indicator. It does not distinguish aromatic types of different H/C ratio). It should be noted that good correlations are obtained between the smoke point of a fuel and its H/C ratio. Also, the smoke point test is considered to be reliable. The crux of the argument is that in the recent specification relaxations allowing reportable fuels, the aromatics content has been given the same weight as smoke point (+ naphthalenes) and luminometer number and that this is unacceptable (14).

The significance of H/C ratio in aviation turbine kerosene has been discussed by Goodger and the diversity of hydrogen content in various kerosene components is well illustrated in Fig. 5 (15). The H/C ratio and hydrogen mass per cent is plotted against boiling point for a series of aromatic compound types and for paraffins. The

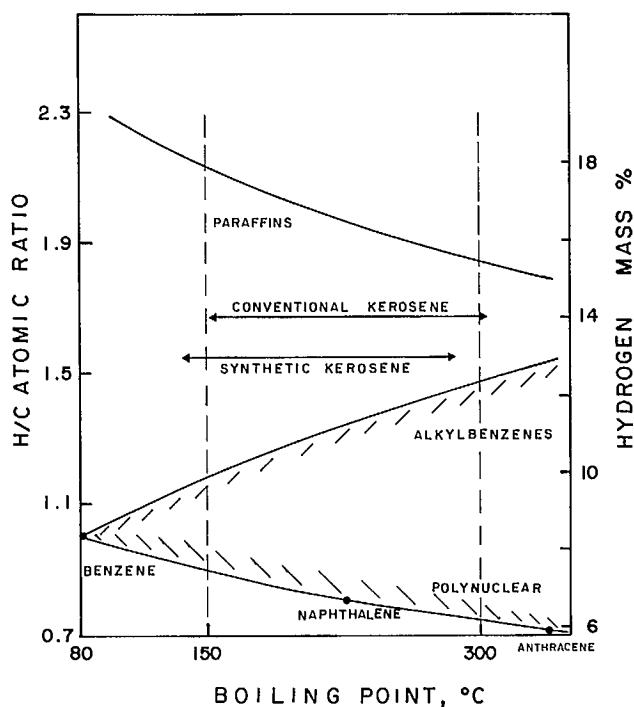


Fig. 5 - Plots of H/C ratio and hydrogen mass per cent versus boiling point for kerosene and fuel components

Source: Reference 15

graph also includes corresponding boiling point ranges for synthetic and conventional kerosenes which have hydrogen contents of 12.9 and 13.9% *m/m* respectively (Table 6). It is apparent that, starting from benzene, with H/C ratio 1.0, the aromatics cover a wide area of the graph and it is possible for alkylbenzenes boiling in the kerosene range to have double the hydrogen content of other kerosene constituents such as naphthalenes.

The above results lend some credence to proposals for alkylating synthetic crude middle distillate fractions using olefins. It is argued that by this means the H/C ratio would be improved thereby producing higher quality jet fuel.

Most experts are clear about the elastomer compatibility problem and the specification limits required. It has been stated that the absolute upper limit for the aromatics content of

fuels used in existing aircraft is 30% (15). Beyond this level it is expected that the elastomer components of fuel systems will degrade. Since the upper limit of aromatics required to protect engine combustor liners is difficult to quantify and the H/C ratio of fuels is now regarded as the important factor, it has been suggested that the aromatics content of Jet A-1 fuel should be allowed to rise above the present 25% V/V maximum.

In a modified CAN 2-3.23 specification it is proposed that a limit of 28% V/V maximum aromatics be allowed together with a smoke point minimum of 18 mm (<3% V/V naphthalenes) which has so far been found acceptable using the "reportable" fuels arrangement. It is claimed that the 18-mm smoke point limit would provide adequate engine hot section life in existing aircraft (14).

It is expected that pressure from refiners to obtain relaxation of specifications will continue since this would allow a greater percentage of synthetic crude to be added to the refinery crude slate. For example, one observer has noted that the recent relaxation in the Jet A-1 specification in Canada, which now accepts 25% aromatics on a "reportable" basis, will allow some refineries to process up to 30% synthetic crude (4).

An alternative solution to the aromatics problem would be for the upgrader or refiner to introduce additional hydrotreating to saturate the aromatics and raise the hydrogen content of synthetic kerosene to the 14% *m/m* which is approximately that of conventional kerosene. This approach could be expensive, raising the price of fuel. A further discussion is included in the section on hydroprocessing.

THE FUTURE FOR HEATING OIL

OVERVIEW

Several recent contributing factors have resulted in a marked decline in the demand for heating oil. These include domestic and industrial energy conservation measures as well as conversions to other forms of heating such as

natural gas and electricity. This downward trend is expected to continue.

The current CAN 2-3.2 specification for heating oil covers seven different fuel types for use in oil burning equipment which can be classified into two groups. Types 00, 0, 1 and 2 fuel oils are primarily for domestic use whereas types 4, 5 and 6 are essentially industrial fuels. Type 2 is the most common domestic fuel and is suitable for use in most atomizing-type burners. Type 00 fuel is intended for use in the Canadian far north where temperatures may fall to -50°C .

Suppliers of heating oil are most concerned with properties associated with fuel burning characteristics. For example, if fuels undergo incomplete combustion and produce excess smoke, then burner efficiency is affected and carbon deposits may block atomizing nozzles. Refiners are able to ensure good fuel burning characteristics by measuring and controlling such properties as viscosity, volatility, density and sulphur content. Other test procedures outlined in the CAN 2-3.6 specification such as flash, cloud and pour point are concerned with transportation and handling.

The performance of heating oil in a domestic burner may be evaluated by a test such as ASTM D2157. Efficiency of combustion is related to clean and relatively smoke-free burning of the fuel and the extent to which the air supply may be reduced without producing an unacceptable smoke level (16).

HEATING OIL FROM SYNTHETIC CRUDE

Since heating oil from synthetic crude is cut from the middle distillate range, its properties are very similar to those of diesel fuel. However, in the production of fuel for heating, a higher end-point might be expected and fuels are likely to have a higher aromatics content.

Comparison of properties of synthetic and conventional distillates which relate to heating fuel burning characteristics indicates that synthetic fuels have less favourable qualities (Table 4). Thus, in synthetic material we find that density, viscosity and aromatics content

are higher. A high aromatics content means that fuels are liable to produce more smoke on burning unless the oxygen supply is increased. Higher fuel viscosities may alter the fuel burner nozzle droplet size in the atomizing process thus affecting the combustion performance.

On the other hand synthetic heating oil has some redeeming properties. Its significantly lower cloud and pour point characteristics makes it useful for blending in winter products and the low sulphur content minimizes corrosion in fuel burners.

INDEX OF BURNABILITY AND SYNTHETIC HEATING FUELS

At present there are no reliable performance tests to adequately assess the burnability of synthetic fuels. However, such tests are needed to establish a fuels combustion performance index which may also be described as an index of burnability (17). The objective of a testing program is to define physical and chemical characteristics of heating fuels which may be considered relevant to combustion performance and to relate these to a burnability index. It is anticipated that part of the testing program would be carried out at the Canadian Combustion Research Laboratory.

It is proposed that a wide range of products be screened and certain critical fuels be selected for intensive testing. The selected fuel matrix would undergo burnability testing using conventional burners together with comprehensive flue gas analysis and temperature monitoring. The analysis of the flue gas content might include oxygen, carbon monoxide, carbon dioxide, oxides of nitrogen, unburnt hydrocarbons, Bacharach smoke number and stack temperature. It is expected that some of the fuels chosen would be close to the limits of burnability.

The testing program would involve a comprehensive examination of certain fuel parameters for each of the products selected. A detailed analysis would include viscosity, density, aniline point, aromatics content by FIA and C^{13} NMR, hydrogen content by NMR and distillation range.

When burnability tests are completed fuels would be ranked on the basis of a particular

burnability performance criterion. Using computer techniques it is hoped that a particular combination of fuel quality parameters may be found that correlates with fuel performance rank. The combination of fuel quality characteristics may then be used as an index of burnability and an acceptable index level can be established (18). The advantage of this system is that it would perhaps allow fuels to exceed some of the present specifications provided most other properties are held well within the limits. Generally, heating oil from synthetic crude is expected to demonstrate an inferior burnability compared with conventional fuels. However, by carrying out the above testing program it may be found that products containing synthetic distillate may demonstrate certain qualities which provide an acceptable index of burnability.

According to an estimate reported in October 1981 by Imperial Oil Ltd., the total Canadian heating oil consumption for the year will fall by 11% compared with that of 1980. In view of this and predictions for the next two decades, it is anticipated that the future problems of heating oil production and supply in Canada will be much less severe than those of diesel and jet fuels.

HYDROPROCESSING OF DISTILLATES AND OTHER SOLUTIONS TO THE AROMATICS PROBLEM

SATURATION OF AROMATICS IN MIDDLE DISTILLATES BY HYDROTREATING

Adding hydrogen to saturate aromatics and convert them to naphthenes has been practised by refineries for some time. The degree of conversion depends on factors such as temperature, pressure, space velocity, catalyst and aromatic type. Kerosene fractions contain more single-ring alkylbenzene types and are easier to saturate than gas-oil streams which have a higher concentration of condensed ring aromatics. Although hydrogenation of aromatics may improve the H/C ratio of synthetic distillates, the disparity of paraffins in these fuel sources is a fundamental problem and increasing the naphthene content may not

necessarily satisfy the combustion requirements of a fuel.

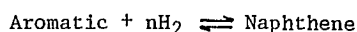
In this respect a distinction should perhaps be made between the requirements of jet and diesel fuels. For jet fuel it has been established that H/C ratio is the most important factor in ensuring good combustion performance and provided that the elastomer compatibility requirement is satisfied, adding hydrogen to synthetic kerosene may produce good quality jet fuel at a cost. On the other hand the cetane number requirements of diesel fuel may not necessarily be met by saturating aromatics.

A number of different hydrotreating processes have been developed and are used throughout the oil industry. The Unisar hydrogenation process for saturating aromatics in distillates to produce jet fuel was introduced in the late sixties by the Union Oil Company (19). Another process - Unifining - is currently used by Suncor Inc., Fort McMurray, to hydrotreat Athabasca bitumen coker distillate streams (10). The hydrotreating of naphtha, kerosene and gas-oil streams removes sulphur, nitrogen and some aromatics. The naphtha unit is operated at 5500 kPa (800 psi) while the kerosene and gas-oil units use more severe conditions with hydrogen pressures at 10 300 kPa (1500 psi). The Suncor hydrotreaters are primarily concerned with sulphur removal and the reduction in aromatics is not monitored on a regular basis. The Unifining catalyst is a proprietary nickel molybdenum type (10). Other notable hydrotreating processes are the Hydrofining process of Exxon and the Ultrafining process of Standard Oil (20).

Most processes employ cobalt-molybdenum or nickel-molybdenum on alumina catalysts. The development of more active and durable catalysts is needed to improve the efficiency of hydrogenation processes. In the hydrotreating of crude distillates, hydrogenolysis reactions involving sulphur and nitrogen removal compete with aromatics saturation. Investigations of the effect of changes in catalyst composition on these processes have been carried out at CANMET's Energy Research Laboratories using coker kerosene distillates from

Athabasca bitumen and unpromoted and promoted MoO_3 /alumina catalysts. Results from these and other recent investigations indicate that different catalytic sites for hydrogenolysis and hydrogenation reactions exist for sulphided $\text{CoO-MoO}_3/\text{Al}_2\text{O}_3$ and the corresponding nickel promoted catalysts (21, 22).

A high degree of aromatics saturation may be achieved using a single-stage hydrotreating unit under severe process conditions, i.e., high pressures and temperatures and long residence times. However, the hydrogenation of aromatics to naphthenes is a reversible reaction and the overall saturation process involves a chemical equilibrium which is temperature dependent:



At high temperatures the degree of aromatics conversion may be limited by the approach to thermodynamic equilibrium. Recent literature shows how aromatics can be saturated in two stages with the second stage operating at a lower temperature which is far removed from equilibrium limitations (23).

Saturation of aromatics in kerosene for the production of jet fuel may require hydrogen

pressures up to 14 000 kPa (~2000 psi) to achieve the required degree of conversion. Such processes may be very costly. An alternative method uses a two-stage process involving initial desulphurization and denitrogenation with removal of H_2S and NH_3 . The aromatics may then be hydrogenated with a more active, but sulphur-sensitive catalyst at pressures as low as 5500 kPa (~800 psi) (24).

IMPROVED UPGRADING OPERATIONS - FLEXICOKING AND HYDROCRACKING

It is argued that improved processes for upgrading oil sands bitumen are required to produce higher quality synthetic crudes and reduce the pressure on downstream refineries. Table 1 shows that material from the Syncrude Project has an API gravity of 32° compared with 41° for conventional crude. Forecasts for future upgrading operations such as the Alsands project are for sweeter crudes with API gravities of 34°-36° (3).

The Imperial Oil Cold Lake Project will be an improved operation and will capitalize on a readily available energy source. Figure 6 presents a schematic representation of a process which has some of the features of the projected Cold Lake Plant (25). The main conversion process

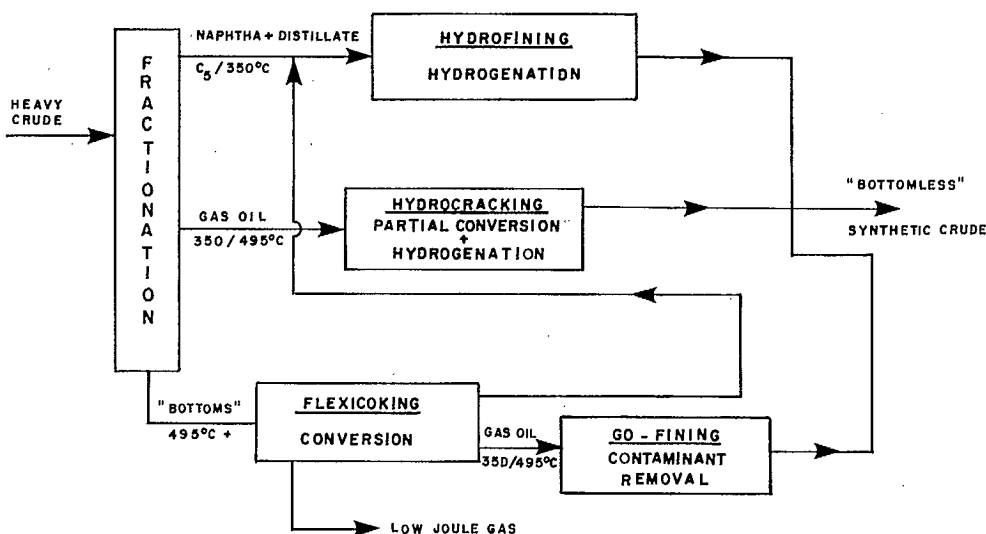


Fig. 6 - Scheme for upgrading heavy crudes

Source: Reference 25

will be Flexicoking, an advanced integrated coking/gasification process for upgrading heavy feedstocks. Apart from producing naphtha, middle distillates, heavy gas-oil and a low sulphur coke gas, the process also has the economic advantage of producing a useable fuel gas (and about 1% petroleum coke) (26).

A hydrocracking unit is also an important feature of the plant. It is designed to achieve partial conversion and hydrogenation of the gas-oil stream obtained after fractionation. The GO-Fining operation will be used to process heavy coker oil by removing contaminants and reducing the aromatics content and a Hydrofining unit will saturate a blend of naphthenes and distillates (20). "Bottomless" synthetic crude will then be blended and pipelined.

IMPROVED DOWNSTREAM OPERATIONS - SCOTFORD REFINERY

In existing conventional refinery operations there is a growing trend to install hydro-

cracking units to cope with a worsening crude quality. These units should allow for a larger synthetic crude intake or residua upgrading. The maximum amount of synthetic crude processable in a conventional refinery at present is about 30%.

The most advanced concept in Canadian downstream processing of synthetic crude is the Scotford refinery which is a joint venture between Shell Canada and Husky Oil. It is due to commence operations in 1984 and will be the first in the world designed to process exclusively synthetic crude oil. It will be capable of utilizing the full range of synthetic crude oil produced from Alberta oil sands and will have a high capacity for producing transportation fuels (27).

The refinery will be located near Fort Saskatchewan, Alberta and will have access to established pipelines. The initial capacity will be 8000 m³/d (50 000 barrels/day). A schematic diagram of the operation is presented in Figure 7 and shows how the standard range of petroleum

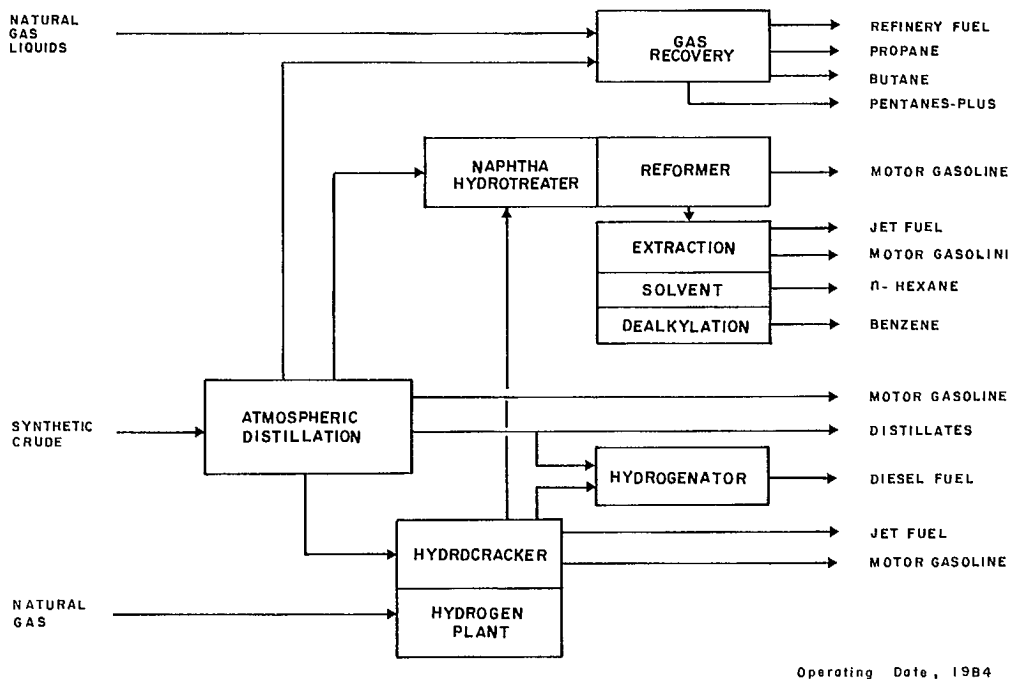


Fig. 7 - Scotford synthetic crude oil refinery
 Operating date: 1984
 Source: Reference 27

products will be produced together with some chemicals.

The most important units are two hydro-cracker trains which will be fed with hydrogen from a plant processing natural gas. Aromatics will be extracted from the reformer stream and de-alkylated to produce 800 m³/d (5000 barrels/day) of benzene for use as a petrochemical feedstock. N-hexane solvent which is produced from this operation will be used in the food industry to extract vegetable oils. The benzene, ethylene and natural gas will be the raw materials for a styrene monomer plant to be constructed adjacent to the refinery. It should be noted that the most difficult refining operation will be to produce diesel fuel of good ignition quality, i.e., minimum cetane number 40. On the other hand, the jet fuel produced is expected to meet current specifications in minimum smoke point and maximum aromatics content.

Although construction of the Scotford refinery will be very costly, some of its concepts will result in favourable economics. The operation will be highly automated using computers and closed circuit TV. A most important economic advantage will be the input of "bottomless" crude which will eliminate the costly conventional processing of residuals.

EXTRACTION OF AROMATICS

Numerous solvent extraction processes have been developed by the petroleum industry. The oldest is the Edeleanu process which uses liquid sulphur dioxide and has long been used to produce smokeless kerosene. Other noteworthy extraction methods are the Shell Sulfolane and Dow Chemical Udex processes (28). It is anticipated that extracting aromatics from synthetic kerosene to produce high quality jet fuel would be costly and create an aromatics marketing problem.

SIDE CHAIN ALKYLATION OF AROMATICS IN SYNTHETIC KEROSENE

Since H/C ratio has been found to be the most significant factor in determining jet fuel

combustion properties, the side chain alkylation of aromatics in synthetic kerosene has been proposed as an alternative to hydrogenation in order to add hydrogen and improve fuel quality. Alkylbenzenes are suitable for these base catalyzed reactions with mono-olefins. Alkali metal catalysts are used in the alkylation of α -hydrogen atoms of the side chain. Olefins suitable for these reactions are ethylene, propylene and to a lesser extent butylenes (29). More research is needed to evaluate the industrial applications of these reactions.

CONCLUSIONS

1. An increase in output from oil sands and heavy crude deposits is projected with synthetic crude comprising about 30% of the total Canadian production by 1990. Middle distillates from synthetic crudes must be produced with a lower aromatics content to satisfy jet and diesel fuel requirements.
2. An increasing Canadian demand for jet and diesel fuels in the next two decades is forecast. It is anticipated that conversion to diesel fuel will increase mainly in the commercial sector. The demand for gasoline is expected to stabilize and that of heating oil to decline.
3. The above developments will exert pressure on refineries and attempts to minimize production costs will be made by working as close to the fuel specifications as possible. It is expected that pressure to relax specifications will continue.
4. Conventional refineries are working close to the limits of flexibility and the intake of refineries that process synthetic crude varies from 20-30%. The limit is usually determined by the amount of jet or diesel fuel which is produced. Some refineries will install new equipment in the 1980's and the maximum syn-crude processable will be about 35%.

5. The Scotford refinery will introduce a new concept and will be dedicated to processing exclusively synthetic crude with a high capacity for producing transportaton fuels. Extensive hydrocracking will be the central feature of this operation.
6. The development of new processing technologies will be required. This will include improvements in hydrotreating, hydrocracking and catalyst performance. It will be difficult to produce diesel fuel from synthetic crude. Adding hydrogen to distillates to produce jet fuel is feasible but costly.
7. Improvements in upstream processing are predicted and a better quality synthetic crude will be produced. Technological advances will be required to achieve this.
8. The extent to which manufacturers of diesel engines and aviation gas turbines will convert to new designs to handle synthetic fuels is unclear. A compromise solution is most likely with some engine modifications and improved distillate quality.
9. It is expected that efforts will continue in Canada to find new unconventional market outlets for synthetic fuels. An example is the use for railway diesel.
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APPENDIX 1

Appendix 1 - Proposed 1982 CGSB standard for diesel fuel

	Type AA	Type A	Type B	ASTM Method
Flash point, °C, min.	40	40	40	D93 or D3828
Cloud point, °C, max.	-48	-34	-23	D2500
Pour point, °C, max.	-51	-39	-30	D97
Kinematic viscosity 40°C, mm ² /s				D445
min.	1.2	1.3	1.4	
max.		4.1	4.1	
Distillation:				
90% recovered, °C, max.	290	315	360	
Water and sediment, % vol., max.	0.05	0.05	0.05	D1796
Total acid number, max.	0.10	0.10	0.10	D974
Sulphur, % mass, max.	0.2	0.5	0.7	D1552
Copper corrosion, 3 h 100°C, max.	No. 1	No. 1	No. 1	D130
Carbon residue (Ramsbottom), on				
10% bottoms, % mass, max.	0.15	0.15	0.20	D524
Ash, % mass, max.	0.01	0.01	0.01	D482
Ignition quality, cetane No., min.	40	40	40	D613

APPENDIX 2

Appendix 2 - Selected Canadian Government Jet A-1/Jet A-2 Specifications CAN 2 - 3.23-M 80

5. DETAIL REQUIREMENTS

EXIGENCES PARTICULIÈRES

NOTICE: The fuels shall comply with the requirements below, the limits of which are absolute, and not subject to correction for tolerances of test methods.

REMARQUE: Le carburant doit être conforme aux exigences suivantes dont les valeurs limites sont absolues et ne peuvent être corrigées pour tenir compte des tolérances des méthodes d'essai.

	Jet A-1		Jet A-2		Test method/ Méthode d'essai		
	Min.	Max.	Min.	Max.			
5.1	Flash point, °C	38	-	33	-	ASTM D56 or/ou D3243	Pointe d'éclair, °C
5.2	Freezing point, °C (Note 1)						Pointe de congélation, °C (Remarque 1)
	Summer - (April-October)	-	-47	-	-45	ASTM D2386	Été - (avril-octobre)
	Winter - (November-March)	-	-47	-	-47		Hiver - (novembre-mars)
		Jet A-1 and/et Jet A-2.					
		<u>Min.</u>		<u>Max.</u>			
5.3	Kinematic viscosity at -20°C, mm ² /s	-		8		ASTM D445	Viscosité cinématique à -20°C, mm ² /s
5.4	Distillation					ASTM D86	Distillation
5.4.1	10% Recovered point, °C	-		204			Après distillation de 10%, °C
5.4.2	50% Recovered point, °C		Report/Indiquer				Après distillation de 50%, °C
5.4.3	90% Recovered point, °C		Report/Indiquer				Après distillation de 90%, °C
5.4.4	Final boiling point, °C	-		300			Pointe d'ébullition final, °C
5.4.5	Distillation residue, % vol	-		1.5			Résidu de distillation, % en vol.
5.4.6	Distillation loss, % vol	-		1.5			Perte à la distillation, % en vol.
5.5	Density, kg/L at 15°C	0.774		0.839		ASTM D1298	Masse volumique, kg/L à 15°C
5.6	Sulphur, % mass	-		0.2		ASTM D1266 or/ou D2622	Soufre, % en masse

	Jet A-1 and/et Jet A-2		Test method	
	Min.	Max.	Méthode d'essai	
5.14 Aromatics, % vol (Note 5)	-	22.0	ASTM D1319	Aromatique, % en vol. (Remarque 5)
5.15 Combustion properties: One of the following				Propriétés de combustion: une des suivantes
1. Luminometer number, (Note 6)	45	-	ASTM D1740	1. Indice photométrique, (Remarque 6)
2. Smoke point, mm	25	-	ASTM D1322	2. Point de fumée, mm,
3. Smoke point, mm, plus Naphthalenes, % vol (Note 7)	20 -	- 3	ASTM D1322 ASTM D1840	3. Point de fumée, mm, plus naphthalènes, % en vol. (Remarque 7)

Note 1: The freezing point limits shall be subject to review before June 30, 1981.

Note 5: Fuel having an aromatics content over 22% by volume, but not exceeding 25% by volume is permitted, provided the supplier notifies the purchaser or Chairman of the Airport Fuel Handling Committee where comingled systems exist, of the volume, destination and aromatic content within 30 d of such shipment.

Note 6: Fuel having a luminometer number less than 40 is permitted, provided the supplier notifies the purchaser, or Chairman of the Airport Fuel Handling Committee where comingled systems exist, of the volume, destination and luminometer number within 30 d of such shipment.

Note 7: Fuel having a smoke point less than 20 mm but not less than 18 mm and a naphthalenes content not exceeding 3% is permitted, provided the supplier notifies the purchaser or Chairman of the Airport Fuel Handling Committee where comingled systems exist, of the volume, destination, smoke point, and naphthalenes content within 30 d of such shipment.

Remarque 1: Les limites du point de congélation doivent faire l'objet d'une révision avant le 30 juin 1981.

Remarque 5: Un carburant ayant une teneur en aromatiques supérieure à 22% en volume, mais ne dépassant pas 25% en volume, est permis, pourvu que le fournisseur avertisse l'acheteur ou le président du comité de manutention des carburants de l'aéroport où existent des systèmes mélangés, du volume, de la destination et de la teneur en aromatiques, dans un délai de 30 d à partir du moment de l'expédition.

Remarque 6: Un carburant ayant un indice photométrique inférieur à 45, sans jamais être inférieur à 40, est permis, pourvu que le fournisseur avertisse l'acheteur ou le président du comité de manutention des carburants de l'aéroport où existent des systèmes mélangés, du volume, de la destination et de l'indice photométrique, dans un délai de 30 d à partir du moment de l'expédition.

Remarque 7: Un carburant ayant un point de fumée inférieur à 20 mm, sans jamais être inférieur à 18 mm, et une teneur en naphthalènes no dépassant 3%, est permis, pourvu que le fournisseur avertisse l'acheteur ou le président du comité de manutention des carburants de l'aéroport où existent des systèmes mélangés, du volume, de la destination, du point de fumée et de la teneur en naphthalènes, dans un délai de 30 d à partir du moment de l'expédition.

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