

2098



Energy, Mines and  
Resources Canada

Énergie, Mines et  
Ressources Canada

## CANMET

Canada Centre  
for Mineral  
and Energy  
Technology

Centre canadien  
de la technologie  
des minéraux  
et de l'énergie

### HYDROPROCESSING OF COAL-DERIVED MIDDLE DISTILLATE

C. FAIRBRIDGE AND J.F. KRIZ  
HYDROCARBON PROCESSING RESEARCH LABORATORY

AUGUST 1985

ENERGY RESEARCH PROGRAM  
ENERGY RESEARCH LABORATORIES  
REPORT ERP/ERL 85-47(J)

ERP/ERL 85-47(j)

# HYDROPROCESSING OF COAL-DERIVED MIDDLE DISTILLATE

C. Fairbridge and J.F. Kriz

Energy Research Laboratories, CANMET,  
Energy, Mines and Resources Canada, Ottawa, K1A 0G1

## ABSTRACT

Coal-derived middle distillate, boiling range 437 to 623 K, was hydrotreated in a fixed bed reactor with a commercial NiO-MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. The feedstock contained predominantly highly-substituted aromatics. The product heteroatom content and aromaticity decreased with increased process temperature or pressure. Aromaticity was proportional to liquid space velocity. Heteroatoms could be effectively reduced at hydroprocessing conditions of 653 K, 10 MPa, and 2 WHSV. Experimentally-derived cetane number was found to be proportional to product aromaticity. Severe hydroprocessing conditions were required to produce diesel fuel of acceptable cetane number.

## INTRODUCTION

The trend towards the processing of heavier feedstocks and the production of synthetic crude focuses attention on distillate quality. Options available for improving the quality of middle

distillates from natural crudes have been discussed (Collins and Unzelman, 1983) and include blending, changing cut points, hydroprocessing, catalytic cracking flexibility and extraction of aromatics. Distillates from oil sands, however, contain more aromatic rings in addition to heteroatoms. Previously, oil sand distillates were found to yield specification diesel fuel only under severe operating conditions with typical hydrotreating catalysts (Wilson et al., 1985). Carbon aromaticity (fa) must be reduced to less than 0.04 to meet cetane number (CN) requirements. The key to cetane improvement in these distillates may involve saturation of monoaromatics (Johnson, 1983). While the atomic H/C ratio can be increased by conversion of aromatics to naphthenes by hydroprocessing, the lack of paraffins in synthetic distillates appears to be a major cause of problems in attaining fuel specifications (Wilson and Kriz, 1984).

Similar problems affect the quality of distillates from coal hydroliquefaction (Kondo et al., 1984a). Although hydroprocessing was found to improve the cetane number, the product still did not meet minimum requirements (Kondo et al., 1984b). On the other hand, lignite-derived liquids were reported to produce good quality diesel (CN = 45) when hydrotreated in a two-stage reactor system (Krichko et al., 1984). An earlier study by Sullivan, O'Rear, and Frumkin (1981) indicated that severe hydroprocessing of coal distillates was required to meet a minimum specification of CN = 40. Recent interest in shale-oil distillates also focussed on questions of product quality in connection with the

reduction of nitrogen and aromatic carbon contents (Thompson and Holmes, 1985). It appears that the feedstock origin as well as the primary upgrading process applied to produce the synthetic crude distillates will significantly affect downstream refining.

The presence of heteroatoms - particularly nitrogen and oxygen - further retrogrades the upgrading of coal-derived liquids. Retardation and catalyst deactivation caused by these compounds might prohibit operation at the severe conditions needed to achieve product quality requirements. Ternan and Brown (1982) indicated that substantial catalyst deactivation occurred on hydroprocessing a wide-cut coal-derived liquid (323-673 K) at the high severity required for heteroatom removal. The present study addresses these questions in an attempt to evaluate the feasibility of hydrotreating coal-derived liquid fractions to produce transportation fuels.

#### EXPERIMENTAL

The middle distillate used in this study was obtained from Ashland Synthetic Fuels Inc. It was derived from Illinois No. 6 coal using HDS 1442-A catalyst with the 200 t/d plant in synthetic crude mode. Feedstock properties are summarized in Table 1. The catalyst used in experimental hydroprocessing was Ketjenfine 840-1.3AQ obtained from Akzo Chemie Nederland bv (18.6% MoO<sub>3</sub> and 3.9% CoO on alumina). The catalyst was sulphided with kerosene spiked with 3 wt % CS<sub>2</sub> at the following conditions:

pretreatment -           WHSV           10 g (feed) g (catalyst)<sup>-1</sup> h<sup>-1</sup>  
                           temperature 473 K  
                           time           2 h

presulphiding -       WHSV           2.5 g g<sup>-1</sup> h<sup>-1</sup>  
                           pressure       3.14 MPa  
                           temperature 523 + 573 + 593 K  
                           H<sub>2</sub>/oil ratio 700 Nm<sup>3</sup> m<sup>-3</sup>  
                           time           5 + 5 + 1 h

The automated reactor system (Zeton Technology Corp.) consisted of a tubular reactor - 1524 x 15.2 mm ID - with a 3.2 mm OD thermo-well. Six k-type indicating thermocouples were located in the catalyst zone ( $\pm 2$  K). The catalyst was diluted with silicon carbide (1:1 v/v) while pre- and post-heat sections were filled with 3 mm Pyrex beads and silicon carbide. Hydrotreating experiments were conducted at 593-673 K, 7-17 MPa, 1-6 WHSV and H<sub>2</sub>/oil ratio 700-1500 Nm<sup>3</sup> m<sup>-3</sup> as summarized below:

Experiment No.	Parameters altered	Catalyst		Diluent SiC (mesh)
		weight (g)	bed height (mm)	
1	T	55.2	900	70-80
2	T, WHSV	39.8	700	50-70
3	T, WHSV	59.6	900	30-50
4	blank, T, P		none	30-50
5	H <sub>2</sub> S, T, P	79.5	900	30-50

The reactor was operated in concurrent downflow, once-through hydrogen mode. Each condition was applied for 24 h with samples collected at 4-h intervals. Samples were stripped at 273 K with nitrogen and phase filtered prior to analysis (Schleicher and

Schuell, No. 595-hy).

Liquid products were analyzed for carbon and hydrogen using a Perkin Elmer 240 elemental analyzer. Nitrogen was determined by Dohrman chemiluminescence and sulphur by Xertex Dohrman System 701. Specific gravities were measured with a Parr DMA35 Densitymeter. PDNA and proton aromaticity (Brown, Ladner, 1960) were determined using a Finnigan 4000 GC-MS and a Varian CFT20 NMR. A Varian XL200 NMR was used to produce carbon-13 NMR spectra of the product liquids (without additional solvent). The nuclear Overhauser enhancement was suppressed by gated-decoupling. A pulse repetition time of 10 s and width of 40° were sufficient to avoid progressive saturation. Structural parameters derived from the spectra according to the procedure of Yoshida, Maekawa, Uchino and Yokoyama (1980) included aromaticity (fa), the ratio of nonbridgehead aromatic carbon to aromatic carbon (Haru/Car), and the degree of aromatic ring substitution ( $\sigma$ ).

$$fa = \text{Car}/\text{total carbon}$$

$$\text{Haru/Car} = (\text{Car}-\text{Cb})/\text{Car}$$

$$\sigma = \text{Cs}/(\text{Car}-\text{Cb})$$

Car: aromatic carbon

Cb: bridgehead carbon (129.2-132.5 ppm)

Cs: substituted aromatic carbon (132.5-167 ppm).

Cetane numbers were determined on a fuel research engine (Waukesha Motor Co.) by a constant compression ratio method.

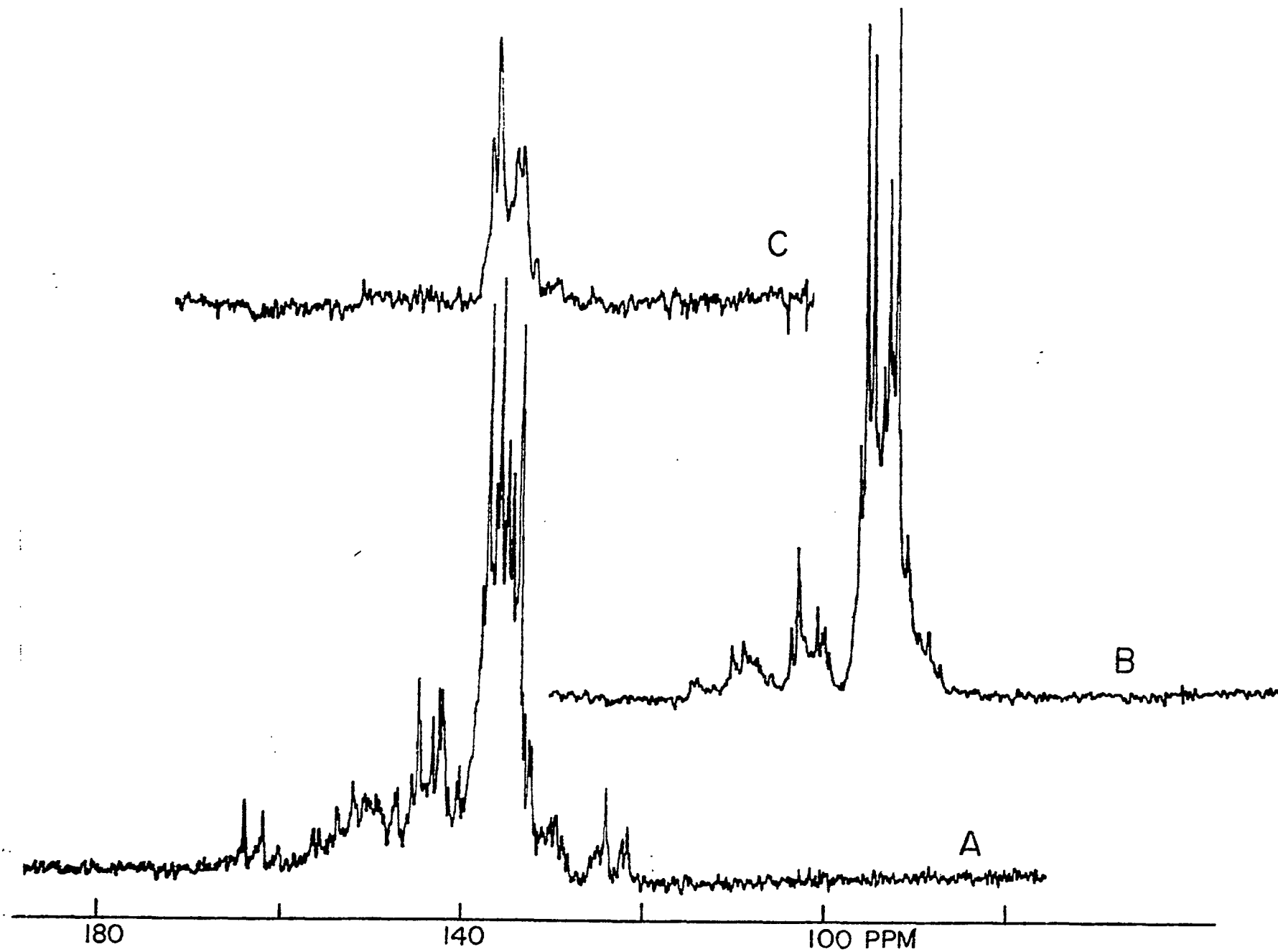


Fig. 1 - Effects of process severity on carbon-13 NMR; A, feed; B, product, 673 K, 1.41 WHSV, 13.90 MPa, offset 40 ppm; C, product, +1 wt % CS<sub>2</sub>, 673 K, 1.07 WHSV, 17.35 MPa.

## RESULTS AND DISCUSSION

Initial experiments were conducted to determine the conditions required to significantly alter the coal liquid properties by hydroprocessing. A molybdenum-nickel catalyst was selected because of the relatively high nitrogen and aromatic carbon contents in the feed. When any process variable other than temperature was altered, the reactor system required at least 4 h before representative liquid samples could be obtained as indicated by sample analysis reproducibility. Changes in temperature required a minimum 12-h stabilization prior to sampling. In general, the specific gravity, heteroatom content and aromaticity decreased with increased temperature or pressure or with decreased liquid space velocity as shown in Table 1.

NMR techniques developed for the direct observation of carbon types can provide valuable structural information (Yoshida et al., 1980; Young and Galya, 1984). Carbon-13 analysis indicated that the number of aromatic rings in an average molecule in the feed was one and that this ring was highly substituted by  $\text{CH}_3$  and/or naphthenic  $\text{CH}_2$  groups (132.5-141.0 ppm chemical shift). The small peak intensity at chemical shift less than 20 ppm which is due to alkyl carbons indicates that the aromatic ring contains few long alkyl side chains. Protonated aromatic carbon (115.0-129.2 ppm) was not predominant. When hydroprocessing severity was increased, the spectra clearly indicated the removal of aromatic carbon which is influenced by the presence of heteroatoms and phenolic groups (148.0-178.0 ppm, Fig. 1). The increase in cycloparaffinic,



methylene bridge and alkyl carbon (24-66 ppm) was also apparent. The Haru/Car ratio and the degree of aromatic ring substitution were 0.95 and 0.92 respectively in the feedstock. These values did not change significantly upon hydroprocessing indicating that little dealkylation had occurred.

Table 1  
Effects of process variables on product analysis

T (K)	P (MPa)	WHSV $g\ g^{-1}\ h^{-1}$	$H_2/O_2$ $Nm^3\ m^{-3}$	Relative Density 15/15°C	% C (wt%)	% H (wt%)	$f_a$	P wt%	O wt%	N wt%	A wt%
feed				0.932	85.94	10.18	0.38	7	9	34	50
599	7.00	1.64	1000	.916	86.33	10.58	.36	8	-	44	47
620	7.00	1.64	1000	.906	87.15	10.94	.33	8	-	45	47
643	7.00	1.64	1000	.893	87.87	11.26	.29	8	-	46	46
598	10.45	2.86	880	.913	86.64	10.75	.35	9	-	44	47
621	10.45	2.86	880	.907	87.17	10.88	.32	8	-	44	48
671	10.45	2.86	880	.884	88.18	11.44	.26	9	-	51	38
671	10.45	1.41	1760	.878	87.96	11.68	.24	10	-	54	32
671	10.45	4.31	880	.893	88.10	11.19	.30	11	-	51	38
671	10.45	5.76	880	.896	87.72	11.15	.33	13	-	54	32
595	10.45	0.90	1200	.894	87.19	11.42	.25	9	-	51	40
595	10.45	1.57	1200	.903	87.08	11.19	.29	9	-	55	36
595	10.45	2.06	1200	.910	86.40	11.01	.35	8	-	45	47
653	7.00	1.41	1200	.882	88.14	11.61	.23	12	-	55	33
653	13.90	1.41	1200	.871	87.32	12.10	.17	10	-	60	30
653	17.35	1.41	1200	.869	87.43	12.23	.15	9	-	60	31
673	10.45	1.41	1200	.867	87.54	12.30	.16	10	-	58	32
673	13.90	1.41	1200	.860	87.04	12.67	.11	10	-	58	32
673	17.35	1.41	1200	.859	87.61	13.03	.05	10	-	59	31

The carbon aromaticity for the hydrotreated coal liquid was found to be directly proportional to the aromaticity as determined from proton NMR ( $f_a'$ ). The experimental relationship is:

$$f_a' = 0.87 f_a + 0.09 \quad (1)$$

Various structural parameters may be calculated with the aid of either proton or carbon-13 NMR results. It was also possible to describe plots of  $f_a$  versus atomic H/C ratio for the liquid products according to the method of Hayamizu and Ohshima (1985). Based upon empirical calculations, the principal reaction occurring on hydroprocessing was hydrogenation of methyl-substituted tetrahydronaphthalene structures.

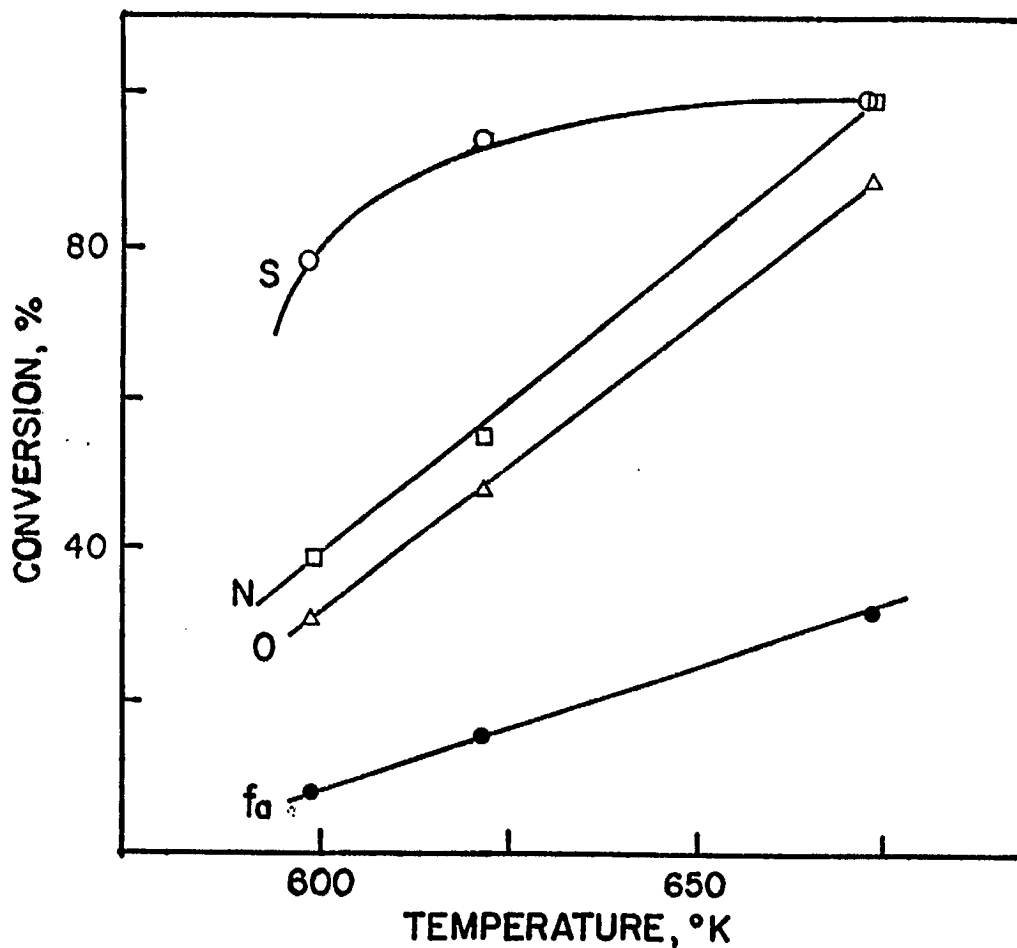


Fig. 2 - Effect of temperature on heteroatom removal and aromaticity conversion at 2.86 WHSV, 10.45 MPa

#### Heteroatom Conversion

The effects of process variables on product sulfur and

nitrogen contents are summarized in Table 2. Sulfur, nitrogen, and oxygen (by difference) were effectively removed at the most severe conditions. Since oxygen content was not determined directly, discussion of catalytic hydrodeoxygenation cannot be highlighted.

Table 2  
Effects of process variables on heteroatom content<sup>a</sup>

Exper. No.	T (K)	WHSV (g g <sup>-1</sup> h <sup>-1</sup> )	Sulfur		Nitrogen	
			Conc. (ug g <sup>-1</sup> )	E <sub>a</sub> <sup>b</sup> (kJ mol <sup>-1</sup> )	Conc. (ug g <sup>-1</sup> )	E <sub>a</sub> <sup>b</sup> (kJ mol <sup>-1</sup> )
feed	-	-	784	-	4400	-
1	599	1.64	193	33	3100	116
	620	1.64	159		1900	
	643	1.64	86		784	
2	598	2.86	174	48	2700	103
	621	2.86	44		2000	
	671	2.86	8		55	
2	671	1.41	21		13	
	671	2.86	8		55	
	671	4.31	52		788	
	671	5.76	88		1200	
3	595	0.90	24		1010	
	595	1.57	38		1878	
	595	2.06	64		2304	

<sup>a</sup> The remaining process conditions are indicated in Table 1

<sup>b</sup> Activation energy for heteroatom removal, first order with respect to initial concentration.

An increase in the extent of heteroatom conversion was observed with increased temperature (Fig. 2) and with decreased liquid space velocity (Fig. 3). The data indicate that sulfur was

more readily removed than nitrogen under these conditions. It is apparent that 99% of the original sulfur and nitrogen can be removed at pressures greater than 10.45 MPa and liquid space velocities less than  $2.86 \text{ g g}^{-1} \text{ h}^{-1}$  at 671 K.

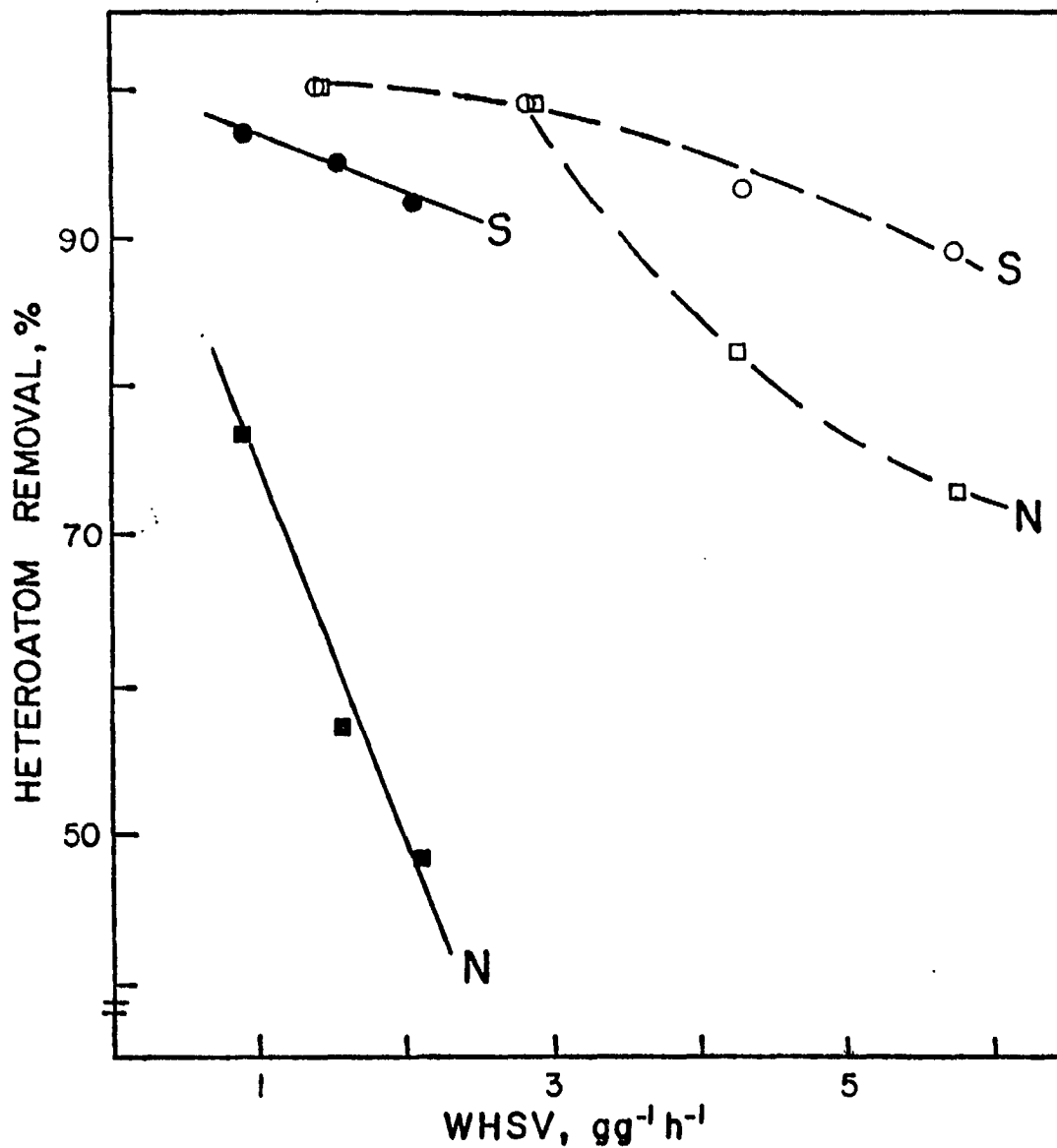


Fig. 3 - Effect of WHSV on heteroatom removal at 671 K, 10.45 MPa (open symbols) and 595 K, 10.45 MPa (closed symbols)

## Aromatics Conversion

At process conditions where 99% of nitrogen and sulphur were removed, only 32% of the aromatic carbon was converted (Fig. 2). Analysis indicated that the olefins and some naphthalenes were converted into benzocycloparaffins whereas monoaromatics were not significantly affected at these conditions.

The effects of liquid space velocity were observed at 671 K (38.9 g catalyst, 700 mm bed height) and 595 K (59.6 g catalyst, 900 mm bed height) at 10.45 MPa and an  $H_2$ /oil ratio of  $885 \text{ Nm}^3 \text{ m}^{-3}$ . As shown in Fig. 4, a decrease in space velocity caused an increase in the conversion of aromatic carbon. The aromaticity was proportional to WHSV, therefore at 10.45 MPa the product liquid would have a minimum fa value of approximately 0.20 at very low space velocity.

The effects of pressure on product quality were observed at 653 and 673 K,  $1.41 \text{ g g}^{-1} \text{ h}^{-1}$  WHSV, and  $1200 \text{ Nm}^3 \text{ m}^{-3}$   $H_2$ /oil ratio (Fig. 5). Aromaticity was inversely proportional to hydrogen pressure. The atomic H/C ratio increased with increasing process pressure. Also included in Fig. 5 are the results of a study at 17.35 MPa using the same feedstock spiked with 1 wt %  $CS_2$ . It was possible to increase the H/C ratio to 1.88 and decrease fa to 0.02 at severe hydrotreating conditions over the  $NiO-MoO_3/Al_2O_3$  catalyst. These results suggest that added  $H_2S$  does not degrade the hydrodenitrogenation or hydrogenation activity of the catalyst.

The results of hydroprocessing on product simulated

distillation are summarized in Table 3 and indicate that the boiling points are reduced on hydrotreating.

Table 3  
P-2887 Simulated Distillation (K)

	Feed	10.45 MPa 1.41 WHSV	13.90 MPa 1.41 WHSV	17.35 MPa 1.07 WHSV + CS <sub>2</sub>
IBP	437	337	339	331
5%	462	387	369	382
10%	473	408	386	404
50%	505	499	468	480
95%	559	568	536	544
FBP	623	608	579	580

The hydrogenation of aromatics is affected by both kinetic and equilibrium phenomena. The equilibrium is expected to shift towards aromatics with increasing temperature and decreasing hydrogen pressure. There are other limitations in connection with the operating conditions. Undesirable cracking reactions complicate product distribution at high temperatures, while higher pressures increase the process cost. Table 1 indicates that although aromaticity is significantly reduced upon hydrotreating, the aromatic carbon conversion is not sufficient at less than 10.45 MPa. This is a high pressure range by commercial standards. Figures 2 and 4 indicate that the equilibrium does not pose limitations within the applied conditions and that a drastic decrease in space velocity or a multistage arrangement would be required to further reduce aromatics. It appears that the conversion of aromatics proceeds more slowly when hydroprocessing

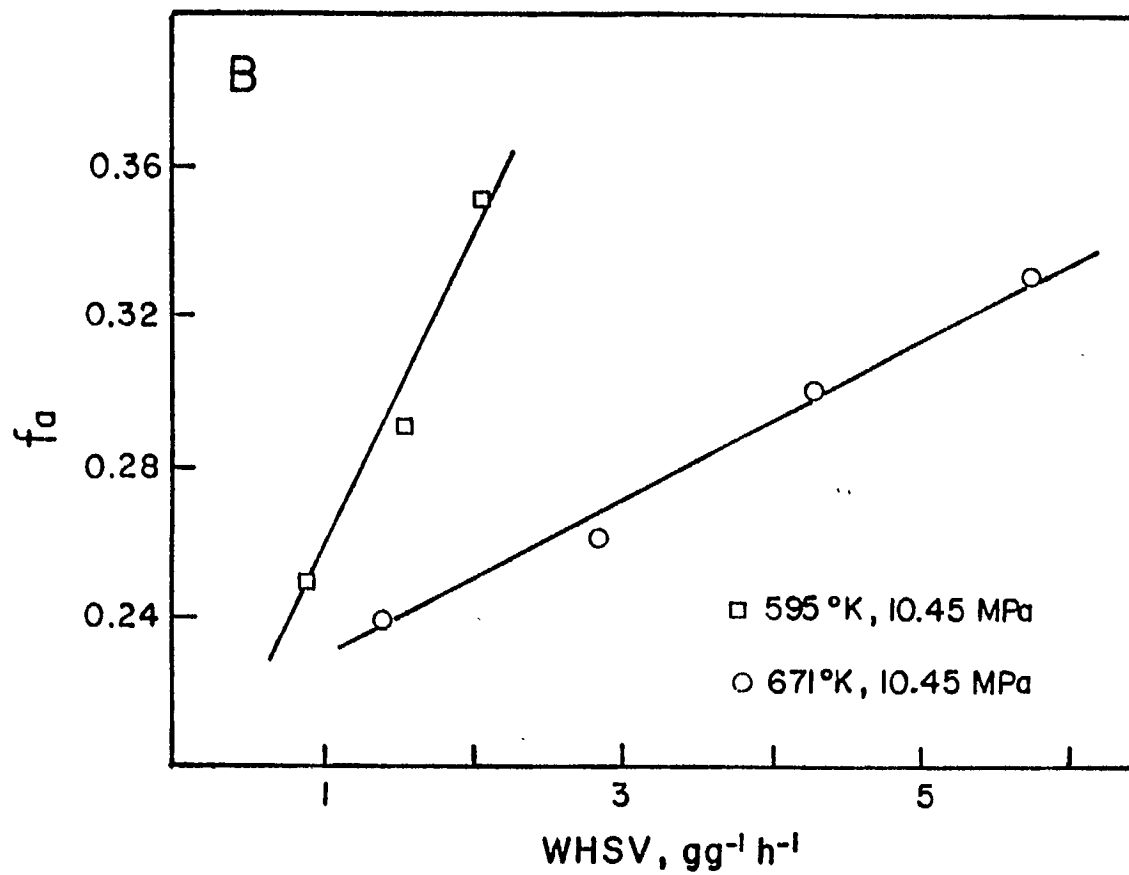
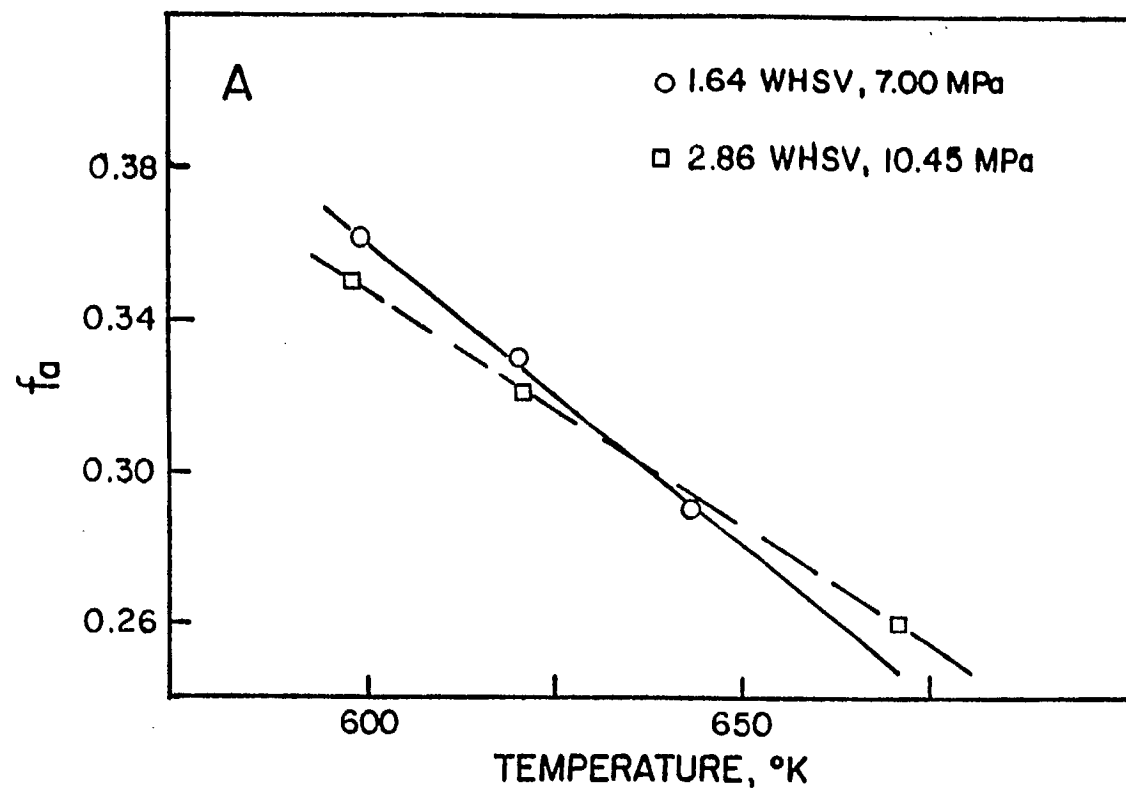


Fig. 4 - Effects of temperature (A) and WHSV (B) on product aromaticity

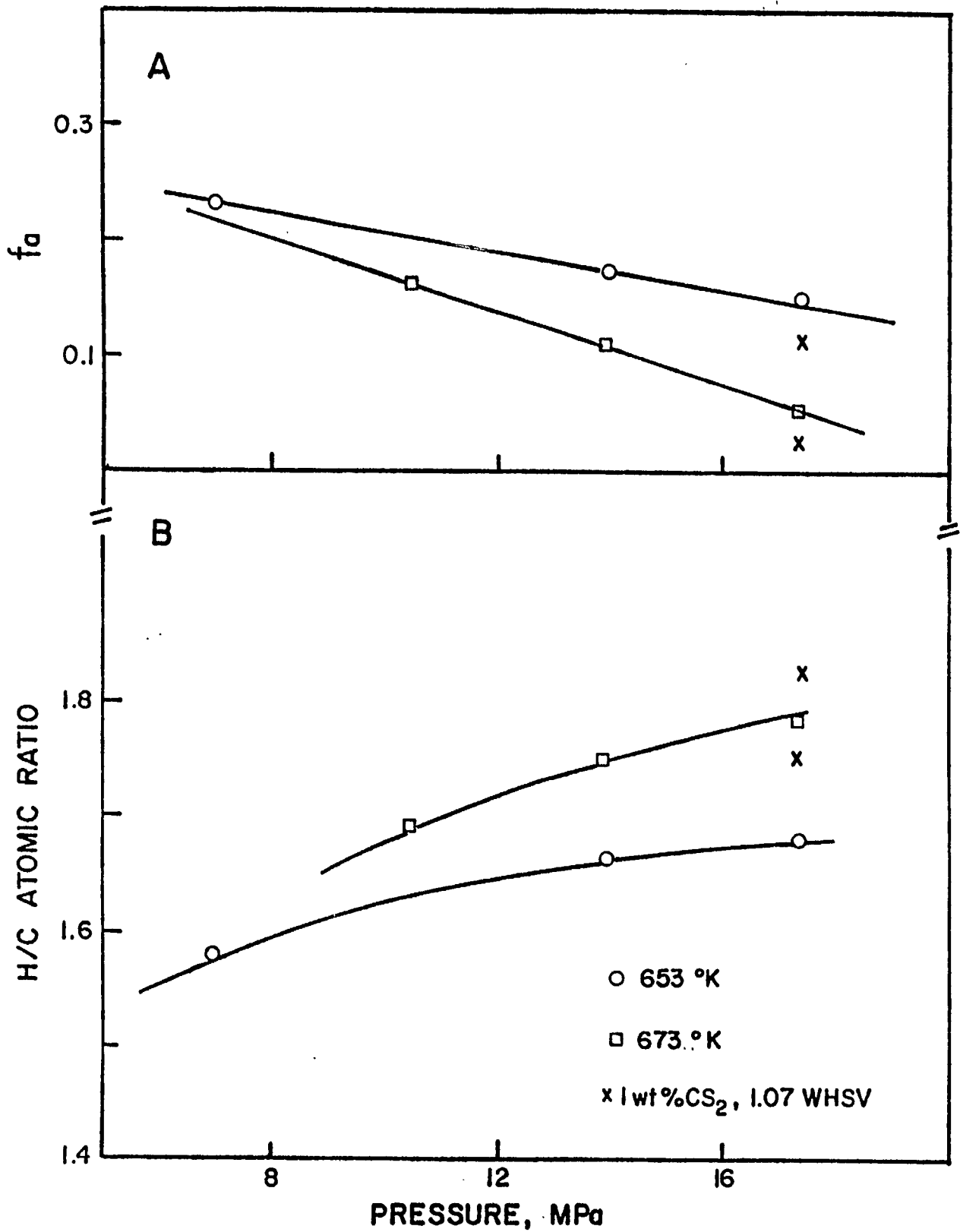


Fig. 5 - Effects of pressure on aromaticity (A) and atomic H/C Ratio (B) at 1.41 WHSV



coal-derived distillates compared with oil-sand distillates. The equilibrium effects observed with oil-sands liquids (Wilson and Kriz, 1984) were not evident in this work. Lower rates of hydrogenation can result from catalyst retardation by oxygen- or nitrogen-containing components or by steric effects related to the high degree of aromatic ring substitution.

The effect of aromatic carbon content on cetane rating is shown in Fig. 6. A decrease in aromaticity produced an increase in cetane number. Minimum cetane specifications would be difficult to obtain using conventional hydrotreating of this coal-derived distillate since, according to these results, complete conversion of aromatic carbon would be required. Hydrogen consumption measurements indicated that  $390 \text{ Nm}^3$  of hydrogen per  $\text{m}^3$  of feedstock was consumed in reducing  $f_a$  from 0.38 to 0.16 and that  $430 \text{ Nm}^3 \text{ m}^{-3}$  was required to give  $f_a = 0.11$ .

The results presented suggest that heteroatoms can be effectively reduced in this particular syncrude distillate through catalytic hydrotreatment at 671K, 10.45 MPa and 2.86 WHSV using a conventional  $\text{NiO-MoO}_3/\text{Al}_2\text{O}_3$  catalyst. Higher operating pressures (18 MPa) would be required to meet the minimum cetane requirement of 40 CN, demanding almost complete saturation of the aromatic components. The cetane requirement may be met by hydrotreating at 14 MPa to reduce  $f_a$  to 0.1 and using a cetane number improver. Sullivan, O'Rear and Frumkin (1981) indicated that the addition of 0.3 wt % octyl nitrate would provide about 7 CN. An alternative

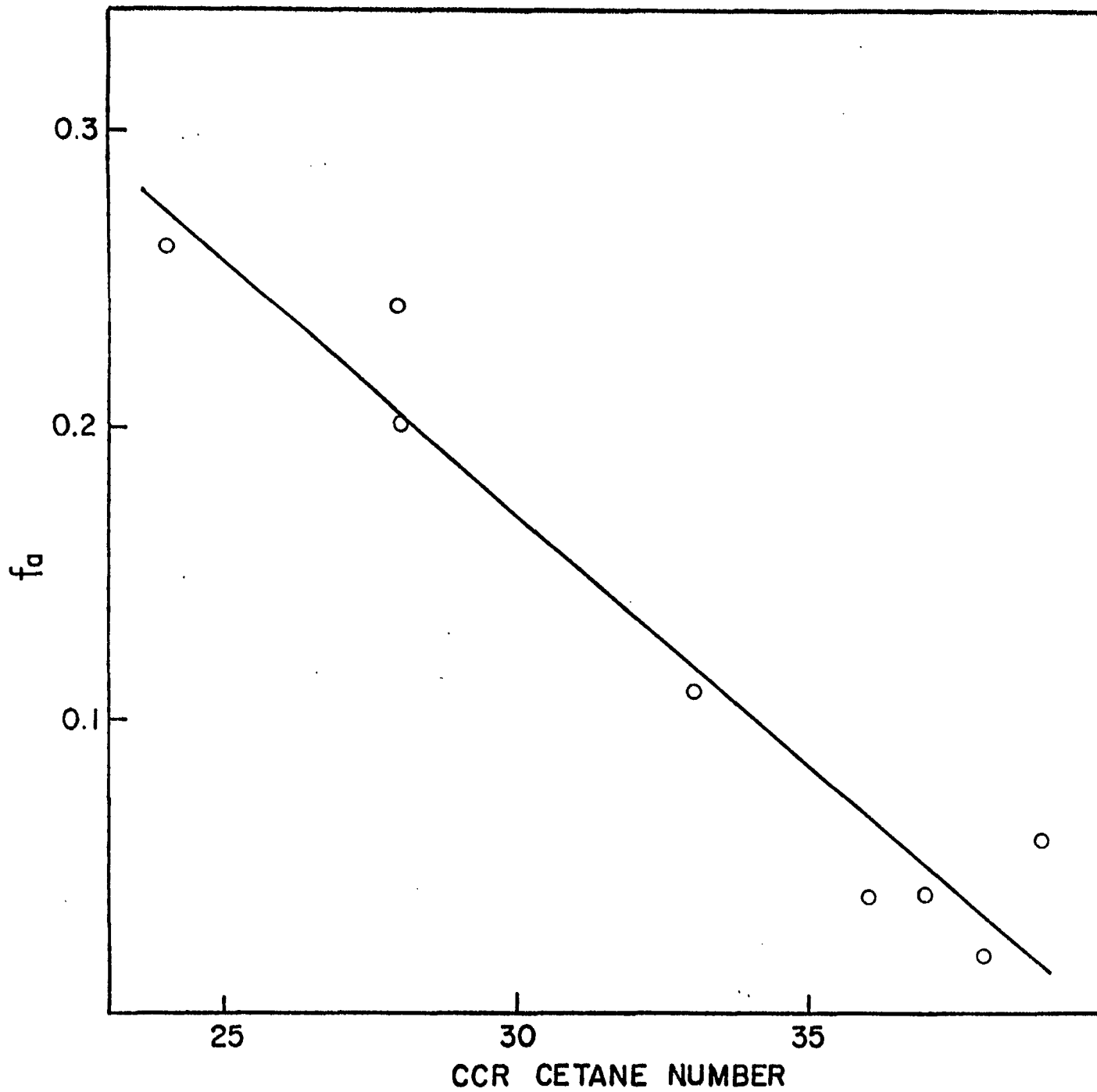


Fig. 6 - Effects of aromaticity on cetane number

approach worth investigating for particular applications would be the use of an active hydrogenation (as opposed to hydrotreating) catalyst which would allow operation at lower severity.

#### ACKNOWLEDGEMENTS

The authors wish to thank Professor G.W. Buchanan, Carleton University, Ottawa, and Dr. T. Yoshida, Government Industrial Development Laboratory, Hokkaido, Japan, for carbon-13 NMR analysis and Mr. N. Kalio of the National Research Council, Fuels and Lubricants Laboratory, for cetane number determinations.

#### REFERENCES

- Brown, J.K. and Ladner, W.R. 1960. A study of the hydrogen distribution in coal-like material by high-resolution nuclear magnetic resonance spectroscopy II Comparison with infrared measurement and the conversion to carbon structure. *Fuel*, 39:87.
- Collins, J.M. and Unzelman, G.H. 1983. Alternatives available to meet diesel cetane quality challenge. OGJ Report, May 30, p 71-78
- Hayamizu, K. and Ohshima, S. 1985. Characteristic diagrams of coal-derived liquids: the correlation between aromaticity and atomic H/C ratios. *Fuel*, 64:130-133.
- Johnson, A.D. 1983. Study shows marginal cetane gains from hydrotreating. OGJ Report, May 30, p 78-82.
- Kondo, K., Ukegawa, K., Matsumura, A., Koguchi, K. and Nakamura, E. 1984a. Hydrotreating of coal derived middle distillate and evaluation of the hydrotreated oil. (Part 1) *J. Japan Petrol. Inst.*, 27:70-73; (Part 2) *J. Japan Petrol. Inst.*; 27:242-246.
- Kondo, T., Ukegawa, A., Matsumura, A., Koguchi, K., Aoyama, H., Ohuchi, H. and Nakamura, E. 1984b. Hydrotreating of coal derived middle distillate and evaluation of the hydrotreated oils (Part 3). *J. Japan Petrol. Inst.*, 27:247-251.

Krichko, A.A., Yulin, M.K., Maloletnev, A.S. and Petrov, Yu.I. 1984. Production of engine fuels from coals of the Kansk-Achinsk basin. Chem. Technol. Fuels & Oils, 20:113-117 (Eng).

Sullivan, R.F., O'Rear, D.J. and Frumkin, H.A. 1981. Converting syncrudes to transportation fuels. Nat. Petrol. Refiners Assoc. FL-81-83.

Ternan, M. and Brown, J.R. 1982. Hydrotreating a distillate liquid derived from subbituminous coal using a sulphided  $\text{CoO-MoO}_3/\text{Al}_2\text{O}_3$  catalyst. Fuel, 61:1110-1118.

Thompson, L.F. and Holmes, S.A. 1985. Effect of multistage hydro-processing on aromatic and nitrogen compositions of shale oil. Fuel, 64:9-14.

Wilson, M.F. and Kriz, J.F. 1984. Upgrading of middle distillate fractions of a syncrude from Athabasca oil sands. Fuel, 63:190-196.

Wilson, M.F., Kriz, J.F. and Fisher, I.P. 1985. Cetane improvement of middle distillates from oil sands by catalytic hydro-processing. Div. Petrol. Chem., Amer. Chem. Soc., Miami Beach Meeting, Apr. 28 - May 3.

Yoshida, T., Maekawa, Y., Uchino, H. and Yokoyama, S. 1980. Derivation of structural parameters for coal-derived oils by carbon-13 nuclear magnetic resonance spectrometry. Anal. Chem., 52:817-820.

Young, D.C. and Galya, L.G. 1984. Determination of paraffinic, naphthenic and aromatic carbon in petroleum derived materials by carbon-13 NMR spectrometry. Liquid Fuels Technol., 2:307-326.