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HYDROTREATING COAL-DERIVED NAPHTHA

C. Fairbridge and B. Farnand  
HYDROCARBON PROCESSING RESEARCH LABORATORY

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## HYDROTREATING COAL-DERIVED NAPHTHA

C. Fairbridge and B. Farnand

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

### ABSTRACT

A coal-derived naphtha was hydrotreated at a range of severities in a bench-scale reactor using a commercial Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. Total sulphur and nitrogen contents were monitored as were the phenolic components. The phenolics represented most of the oxygen contribution. Very severe operating conditions were required for removal of these heteroatoms. The relative rate of heteroatom removal at 10.45 MPa and space velocity less than  $1.25 \times 10^{-3}$  g feed per gram catalyst second was found to be:

oxygen > sulphur > nitrogen

where only phenolic oxygen was measured. The rate of removal of the phenolic compounds decreased in the order:

phenol > m-cresol > p-cresol > o-cresol >  
dimethyl- and o-ethyl-phenols

at the same conditions. The total molar content of phenol, benzene and cyclohexane were found to be constant although the relative concentrations varied with operating conditions.

## INTRODUCTION

To implement coal-derived liquids from direct coal liquefaction or coprocessing as transportation fuels, their susceptibility to upgrading by existing refining processes must be investigated. One strategy for upgrading coal naphtha is catalytic reforming once catalyst deactivating components have been removed. Heteroatoms such as sulphur, nitrogen and oxygen have been identified as reformer catalyst poisons. Several studies concerning the upgrading of coal-derived synthetic crudes using conventional or modified conventional refining processes have been completed (deRosset et al., 1979; O'Rear et al., 1981; Robinson et al., 1982; Krichko et al., 1984; as examples). Hydroprocessing studies of coal-derived naphtha to remove sulphur and nitrogen and to increase the final aromatic carbon content have also been reported (Jankowski et al., 1982; Armstrong, 1982; Robinson et al., 1983; Fairbridge, 1983a; Asim et al., 1983).

Hydrogenolysis of the carbon-oxygen bond and the hydrogenation of heteroaromatic rings have been investigated by the use of model compounds (Bredenberg et al., 1982; Weigold, 1982; Furimsky, 1983a; Odeburmi and Ollis, 1983) and actual feedstocks (Furimsky, 1978; Yoshida et al., 1983; Elliot, 1983; Li et al., 1984). The chemistry of hydrodeoxygenation has been reviewed (Furimsky, 1983b). For phenolic oxygen removal, it appears that the catalyst and reactor system dictate the requirement for prior aromatic ring saturation. The fate of phenols during hydroprocessing is par-

ticularly important since they constitute most of the oxygen content of a coal-derived naphtha. Presumably, the yield of higher quality components from phenol hydrogenation and the hydrogen consumption can be controlled by reaction conditions.

This investigation considers the removal of heteroatoms from a coal-derived naphtha with particular emphasis on the phenolic components. A commercial Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst was used in a bench-scale reactor to observe the effects of process variables on hydrogenation and heteroatom removal at severe hydroprocessing conditions. As a result of this study, information regarding the fate of phenols and their relative reactivity for hydrodeoxygenation has been obtained.

#### EXPERIMENTAL

The feedstock was an H-Coal naphtha supplied by Ashland Synthetic Fuels, Incorporated. It was derived from Illinois No. 6 coal, processed in a 200 t/d demonstration plant operated in the synthetic crude mode of operation using HDS 1442-A (American Cyanamid, Co-Mo/Al<sub>2</sub>O<sub>3</sub>). The boiling range of the naphtha was 312 to 500 K (ASIM D-2887).

In this study, the 305 mm x 12.7 mm ID tubular reactor was operated with concurrent downflow of hydrogen and naphtha. The catalyst, Harshaw HT 400 E (15% MoO<sub>3</sub> and 3% CoO on gamma alumina), was presulfided at atmospheric pressure for 1 h at 503 K and 2 h at 673 K using 10% hydrogen sulfide in hydrogen at 400 mL min<sup>-1</sup>.

Experiments were conducted at 10.45 and 13.90 MPa from 633 to 693 K with liquid space velocity (SV) from 3 to  $14 \times 10^{-4}$  g feed per gram catalyst second ( $\text{g g}^{-1} \text{s}^{-1}$ ). The ratio of hydrogen gas flow to liquid feed rate was maintained at  $880 \text{ Nm}^3 \text{ m}^{-3}$  for all experiments. The catalyst bed depth was 200 mm with 16-g loadings. The 3.2-mm catalyst extrudates were diluted with silicon carbide approximately 1:1 by volume and, in one case, the catalyst was ground from 74 to 149  $\mu\text{m}$  particle size and diluted. Each experimental condition was applied for 8 h and samples were taken at 2-h intervals. Prior to analysis, samples were placed in an ice bath and stripped by a helium purge for 5 min and then phase filtered using Schleicher and Schuell no. 595 - hy phase separation membranes.

Liquid products were analyzed for carbon, hydrogen and nitrogen using a Perkin Elmer 240 elemental analyzer. Sulphur was determined by the Wickbold technique and low level nitrogen by Dohrman microcoulometry. Hydrocarbon content analysis (wt % paraffins, olefins, naphthenes, and aromatics, - PONA) was performed using a Finnigan 4000 GC-MS instrument with an INCOS data system. Quantitation of the n-alkanes, aromatics, cyclohexanes, and phenols was performed by gas chromatography (Varian 6000) using a 30-m DB-1 capillary column (J & W Scientific) and a 30-m bonded 20k MW polyethylene glycol capillary column (Supelco). Retention times were calibrated by doping the naphtha samples with pure components and by GC-MS. The non-polar DB-1 column was used to determine the n-alkane content and the polyethylene column was

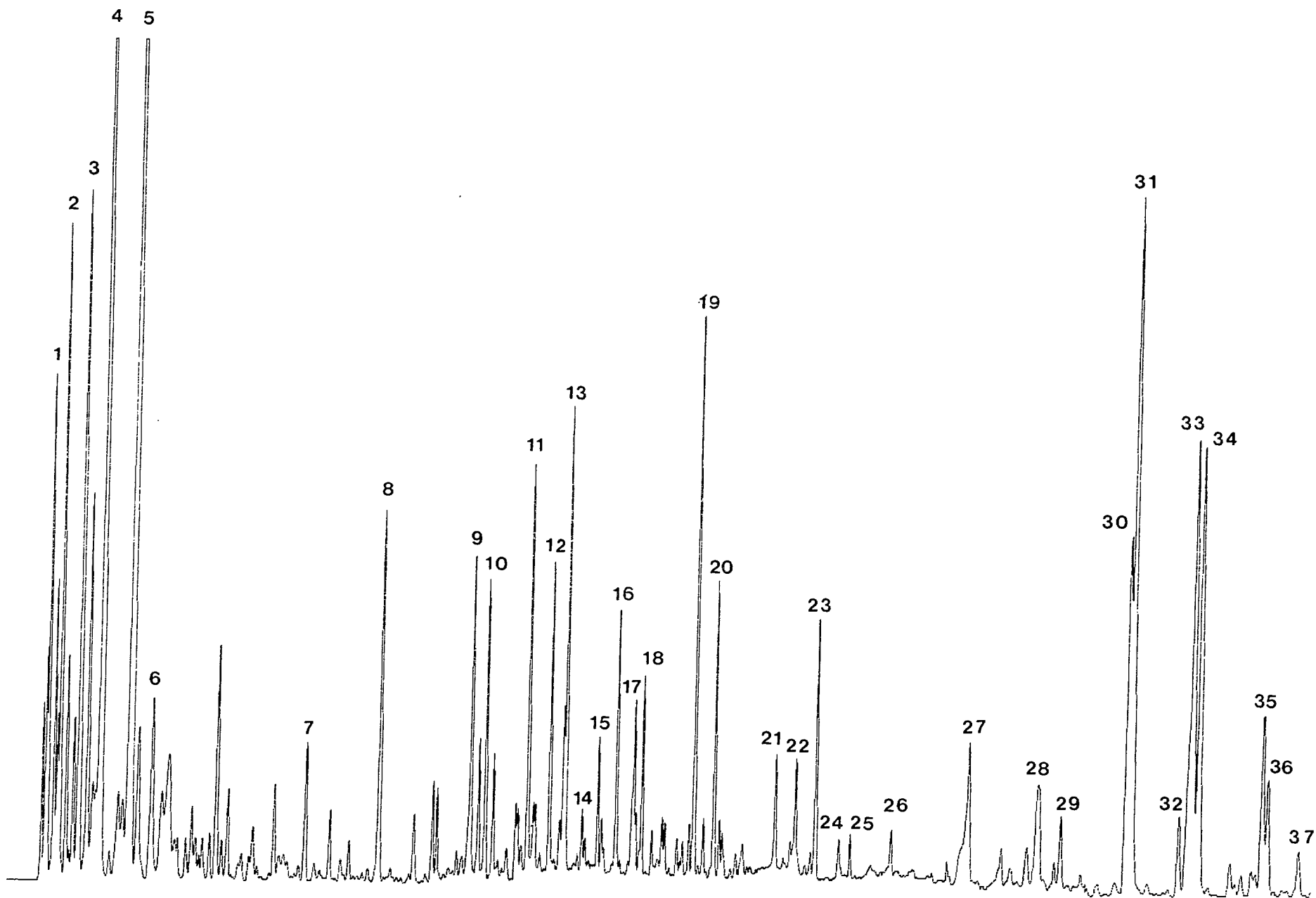


Fig. 1. Capillary GC chromatogram of untreated naphtha on bonded Carbowax 20 m column (peak identification in Table 1).

Table 1

Chromatographic peak identification in coal-derived naphtha<sup>a</sup>

Peak no.	Component	Wt %	Peak no.	Component	Wt %
1	n-pentane	2.38	20	methylindane	0.72
2	n-hexane	3.05	21	"	0.32
3	n-heptane	5.02	22	"	0.39
4	cyclohexane	8.16	23	methyltetra-	
5	methylcyclohexane	8.96		hydronaphthalene	0.63
6	n-octane	1.46	24	"	0.14
7	benzene	1.43	25	"	0.90
8	toluene	5.28	26	"	0.11
9	mesitylene	1.02	27	naphthalene	0.30
10	pseudocumene	1.34	28	methylnaphthalene	0.10
11	ethylbenzene	2.17	29	2,6-dimethylphenol	0.08
12	1-methyl-2-ethyl-		30	o-cresol	1.30
	benzene	0.87	31	phenol	1.90
13	m-xylene	1.72	32	o-ethylphenol	0.18
14	cumene	0.23	33	p-cresol	1.51
15	p-xylene	0.10	34	m-cresol	1.73
16	o-xylene	1.11	35	2,3-dimethylphenol	0.12
17	diethylbenzene	0.21	36	3,5-dimethylphenol	0.26
18	n-butylbenzene	0.53	37	3,4-dimethylphenol	0.24
19	indane	1.32	Total		57.29

<sup>a</sup> 30 m x 0.25  $\mu$ m ID Supelcowax 10 capillary column; split injection; 308 K x 7 min, 5 K min<sup>-1</sup> to 523 K x 15 min; FID detector; He carrier with N<sub>2</sub> makeup gas.

used for the other components. A chromatogram of the feed is shown in Fig. 1 along with the peak identification in Table 1. All of the oxygen content was assumed to be contributed by the phenolic components. This was confirmed in the feed where total oxygen analysis by combustion (Perkin Elmer 240) indicated 1.0 wt % oxygen compared to 1.09 wt % oxygen calculated by chromatography. Benzofurans and dibenzofurans may not be present in large concentrations since the feed has already been exposed to a hydrotreating catalyst at high hydrogen pressure in the H-Coal process. Catalysts were analyzed by nitrogen adsorption and mercury porosimetry (Micromeretics Autopore 9200).

#### RESULTS AND DISCUSSION

The effects of catalyst dilution on the naphtha product are summarized in Table 2. It is apparent that the heteroatom content decreases with decreasing particle size. The results obtained with ground catalyst and silicon carbide, 74 to 149  $\mu\text{m}$  size range, indicate 25  $\mu\text{g g}^{-1}$  sulphur and  $<1 \mu\text{g g}^{-1}$  nitrogen in the liquid product. This sulphur concentration is probably below the limits of the instrumental method used for detection so that the removal of heteroatoms is greater than 99%. A similar study (Asim et al., 1983) indicated the absence of any mass-transfer or pore-diffusion limitations in the hydrotreatment of SRC-I naphtha for the removal of nitrogen and oxygen heteroatoms with an effectiveness factor greater than 0.92 for similarly diluted catalyst beds. Further



studies were therefore conducted using the catalyst extrudates diluted with 74 to 149  $\mu\text{m}$  particles of silicon carbide.

As indicated in Table 2 for hydroprocessing at 653 K, 10.45 MPa and  $6.83 \times 10^{-4} \text{ g g}^{-1} \text{ s}^{-1} \text{ SV}$ , the H/C atomic ratio was approximately 1.73 for the ground and extruded catalyst runs and the product relative density was essentially constant at 0.7956. Hydrocarbon type analysis by GC-MS indicated 30% paraffins and 54% naphthenes in the products compared with 29% and 44% respectively in the H-Coal naphtha. Phenol and methyl and ethyl-substituted phenols were not detected by GC-MS in the products under these conditions and were presumably converted to monocyclic naphthenes. The effects of catalyst dilution, therefore, were less obvious for hydrocarbon type analysis than heteroatom content.

The main purpose in diluting the catalyst bed was to examine naphtha hydroprocessing using a commercial extruded catalyst and a small reactor system without having to grind the catalyst (3.2 mm diameter x approximately 6 mm length). This would facilitate future catalyst comparison studies. The results presented in Table 2 are the average of four experiments. During the course of this study, it was observed that replicate experiments with diluted catalyst beds gave reproducible results. Experiments performed using only the extruded catalyst gave not only poor heteroatom conversions, but also very poor reproducibility. The reasons for better reactor performance using diluted catalyst beds remain unclear, however, temperature control was noticeably improved - both along the catalyst bed and from one loading to another. For

these reasons, catalyst bed dilution with silicon carbide particles is recommended for hydroprocessing studies using small bench-scale reactor systems.

The effects of temperature were examined from 613 to 693 K at 10.45 and 13.90 MPa hydrogen pressure. The influence of temperature on heteroatom removal is shown in Fig. 2. Reaction rate constants were derived for heteroatom removal using a reaction order of one with respect to initial concentration assuming plug flow. This resulted in the following equation for reaction rate constants:

$$k = SV \cdot \ln (C_0 / C) \quad (1)$$

where  $C_0$  is the initial heteroatom concentration and  $C$ , the concentration in the hydrotreated product. The results for apparent activation energies and pre-exponential factors are also given in Table 3.

Examination of Table 3 indicates that the heteroatom content of hydrotreated naphtha decreased with increased treatment temperature. It is evident that complete removal of these heteroatoms (>99%) required 673 K and 13.90 MPa hydrogen pressure in order to produce a product meeting reformer feedstock specifications. These are very severe operating conditions. There is considerable evidence, however, to indicate that the reforming step would produce high quality gasoline rich in aromatic content and would liberate sufficient hydrogen to balance

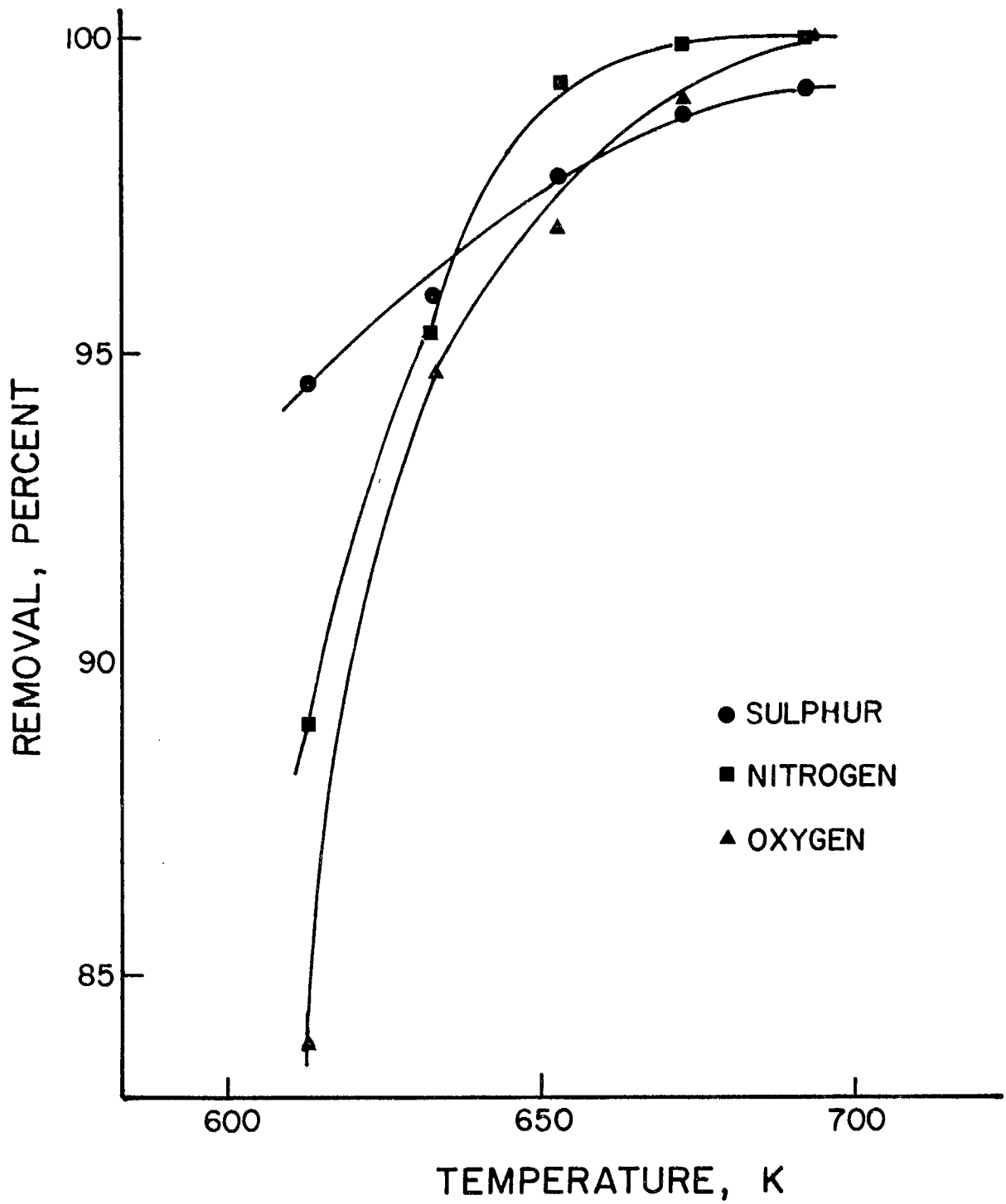


Fig. 2. Effect of temperature on heteroatom removal at 13,90 MPa,  $6.83 \times 10^{-4} \text{ g g}^{-1} \text{ s}^{-1}$  SV and  $880 \text{ Nm}^3 \text{ m}^{-3} \text{ H}_2$ /feed ratio using Co-Mo/Al<sub>2</sub>O<sub>3</sub>.

Table 2  
Effects of catalyst dilution<sup>a</sup>

	Hydrotreated product analysis				
	Feed	Silicon carbide ( $\mu\text{m}$ )			Ground catalyst +SiC( $\mu\text{m}$ )
		297-210	210-177	149-74	149-74
Atomic H/C	1.61	1.72	1.73	1.75	1.73
Sulfur( $\mu\text{g g}^{-1}$ )	3000	224	85	37	25
Nitrogen( $\mu\text{g g}^{-1}$ )	2400	10	28	2	<1
Relative density (288 K)	0.8195	0.7952	0.7952	0.7959	0.7959
P (wt %)	29	30	31	30	30
N (wt %)	44	52	53	54	54
A (wt %)	26	17	15	15	15

<sup>a</sup> 16 g Co-Mo/Al<sub>2</sub>O<sub>3</sub>, 10.45 MPa, 653 K,  $6.83 \times 10^{-4} \text{ g g}^{-1} \text{ s}^{-1}$  SV and  $880 \text{ Nm}^3 \text{ m}^{-3} \text{ H}_2/\text{feed}$  ratio.

Table 3  
Effect of process temperature on product heteroatom content

T (K)	P (MPa)	SV x $10^{-4}$ ( $\text{g g}^{-1} \text{ g}^{-1}$ )	S ( $\mu\text{g g}^{-1}$ )	N ( $\mu\text{g g}^{-1}$ )	O ( $\mu\text{g g}^{-1}$ )
633	10.45	6.44	287	227	656
653	10.45	6.88	85	28	159
673	10.45	7.11	54	1	43
693	10.45	6.88	44	<1	-
$E_a$ (kJ mol <sup>-1</sup> )			39	115	69
A (s <sup>-1</sup> )			2.8	$4.4 \times 10^6$	$9.0 \times 10^2$
613	13.90	6.83	163	264	1769
633	13.90	6.83	123	112	580
653	13.90	9.11	65	16	330
673	13.90	6.83	37	1	8
693	13.90	6.83	25	<1	-
$E_a$ (kJ mol <sup>-1</sup> )			23	73	78
A (s <sup>-1</sup> )			0.2	$2.4 \times 10^3$	$6.0 \times 10^3$

that used in hydrotreating (de Rosset et al., 1980; Jankowski et al., 1982; Robinson et al., 1983). The effect of increased operating pressure was also apparent. An increase from 10.45 to 13.90 MPa resulted in a significant decrease in the heteroatom content of the product. Compared with 673 K, hydroprocessing at 693 K produced a liquid with lower monocyclic naphthene and paraffin contents and higher aromatics content. This may be attributed to dehydrogenation reactions at the higher temperatures and pressures.

The value of  $SV$  was varied from  $3.41 \times 10^{-4}$  to  $13.66 \times 10^{-4}$   $\text{g g}^{-1} \text{s}^{-1}$  at 10.45 MPa and 633 and 653 K (Table 4). The reaction order of one was verified by the linear plots of  $\ln$  (fraction unreacted) versus  $SV$  for nitrogen and oxygen removal (Fig. 3). The data for oxygen exhibit more scatter than those for nitrogen. This reflects the fact that the oxygen analysis by gas chromatography is less reproducible than that for nitrogen for low levels of heteroatoms ( $\pm 60 \mu\text{g g}^{-1}$  for oxygen as opposed to  $\pm 1 \mu\text{g g}^{-1}$  for nitrogen). The data for sulphur conversion do not appear to follow simple first order reaction kinetics and the apparent activation energy for sulphur removal was low (Table 3). The rate constants were therefore calculated from integration of the mass balance over the reactor assuming plug flow:

$$k = SV \cdot 1/(n-1) \left[ (1/S^{n-1}) - (1/S_0^{n-1}) \right] \quad (2)$$

and using a pseudo reaction order ( $n$ ) of 1.65 (de Bruijn, 1977).

Table 4

Effect of liquid space velocity on the analysis of  
coal-derived naphtha hydrotreated at 10.45 MPa

SV x 10 <sup>-4</sup> (g g <sup>-1</sup> s <sup>-1</sup> )	-	3.41	6.83	10.24	13.66	3.41	6.83	10.24	13.66
T (K)	-	633	633	633	633	653	653	653	653
S (μg g <sup>-1</sup> )	3000	30	39	228	405	105	89	36	143
N (μg g <sup>-1</sup> )	2400	21	273	344	1900	3	67	228	1400
O (μg g <sup>-1</sup> )	10941	129	615	957	9686	5	216	247	4192
2,6-dimethyl- phenol (μg g <sup>-1</sup> )	828	207	240	283	1112	-	-	262	501
o-cresol (μg g <sup>-1</sup> )	12970	175	1292	2015	13052	252	252	460	7610
phenol (μg g <sup>-1</sup> )	18968	171	813	1305	19086	300	161	449	7522
o-ethylphenol (μg g <sup>-1</sup> )	1770	-	346	536	1618	100	100	201	937
p-cresol (μg g <sup>-1</sup> )	15060	184	335	606	9024	195	119	162	3170
m-cresol (μg g <sup>-1</sup> )	17320	130	693	1256	15162	303	217	271	5740
3,5-dimethyl- phenol (μg g <sup>-1</sup> )	2580	-	137	205	2298	-	-	137	1056
3,4-dimethyl- phenol (μg g <sup>-1</sup> )	2440	-	228	285	261	114	250	-	1047

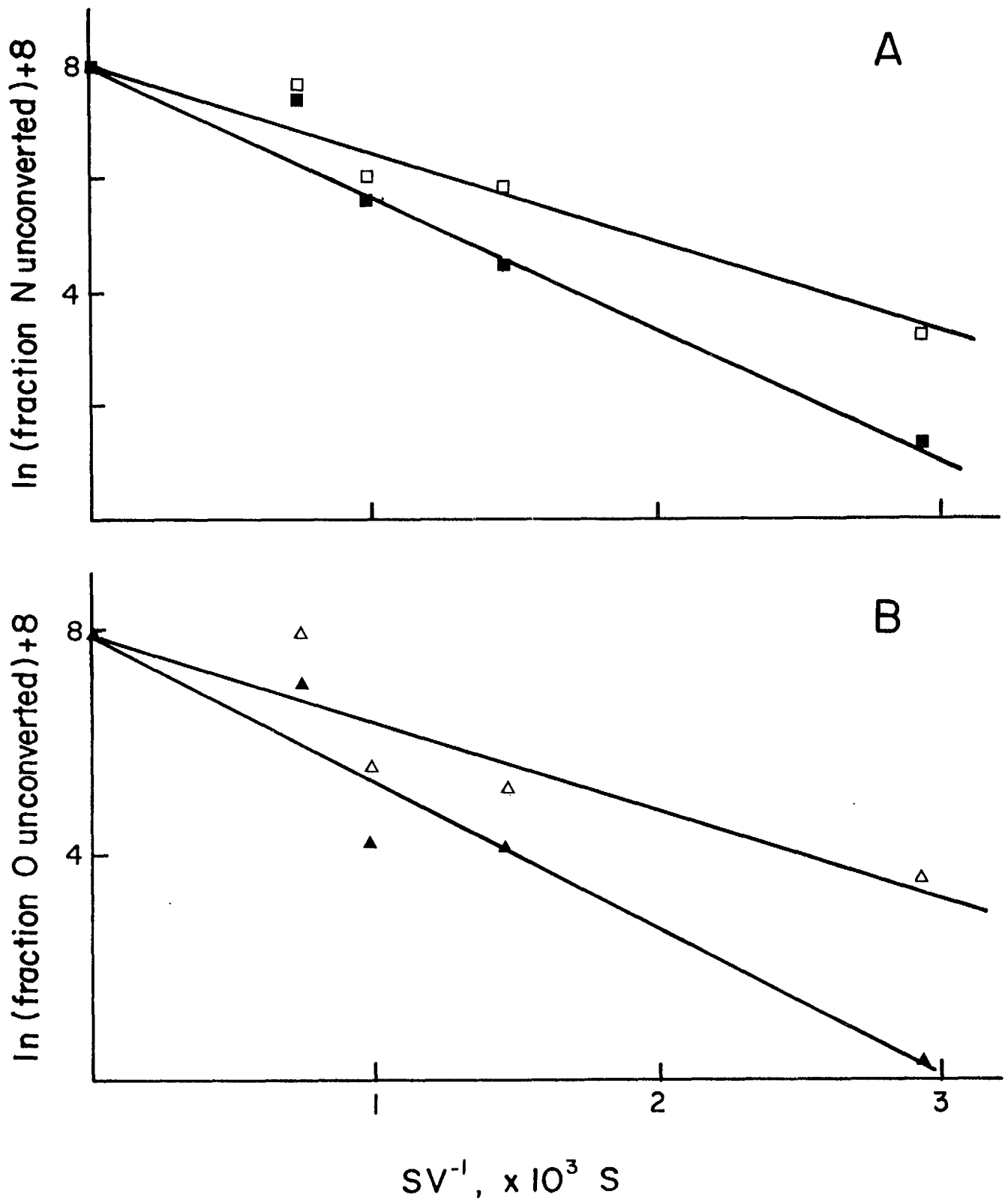


Fig. 3. Conversion of nitrogen (A) and oxygen (B) in coal-derived naphtha at 10.45 MPa, 633 K (open symbols) and 653 K (closed symbols) using Co-Mo/Al<sub>2</sub>O<sub>3</sub>.

When plotted in Arrhenius fashion, the data yielded values for the apparent activation energy for sulphur removal of 87 and 53  $\text{kJ mol}^{-1}$  at 10.45 and 13.90 MPa, respectively. The apparent activation energy for heteroatom removal generally decreased with increased hydrogen pressure (Table 3). Since the results for oxygen removal are less precise, the change in activation energy with pressure shown in Table 3 has little significance.

The data may also be plotted as the rate of heteroatom removal (gram heteroatom removed per gram catalyst second) against space time where space time is the inverse of space velocity ( Fig. 4). The rate of removal is given by:

$$r = (C_0 - C) \cdot SV \quad (3)$$

where  $(C_0 - C)$  gives the amount of heteroatom removal (gram heteroatom per gram feedstock). This plot clearly shows a maximum nitrogen and oxygen removal rate at a residence time of approximately 800 s, corresponding to a space velocity of  $1.25 \times 10^{-3}$  g feed per gram catalyst second.

The data for sulphur, however, show a gradual increase in rate of removal with decrease in residence time. Previous studies (Asim et al., 1983) have indicated possible mass-transfer limitations in sulphur removal and anomalous results with sulphur compared to nitrogen and oxygen removal. The present study indicates that at 10.45 MPa and using an SV less than  $1.25 \times 10^{-3}$  g per gram catalyst second, the rates of heteroatom removal decrease in the



order:

oxygen > sulphur > nitrogen

where the measured oxygen compounds were phenolic in nature. Comparisons of these reactivity data with previous studies must take into account the different feedstocks and reactor systems. For example, basic nitrogen-containing compounds were found to inhibit the reactivity of phenolic-OH (Krishnamurthy and Shah, 1982) and self inhibition among phenolic oxygen compounds was thought to be significant (Li et al., 1984).

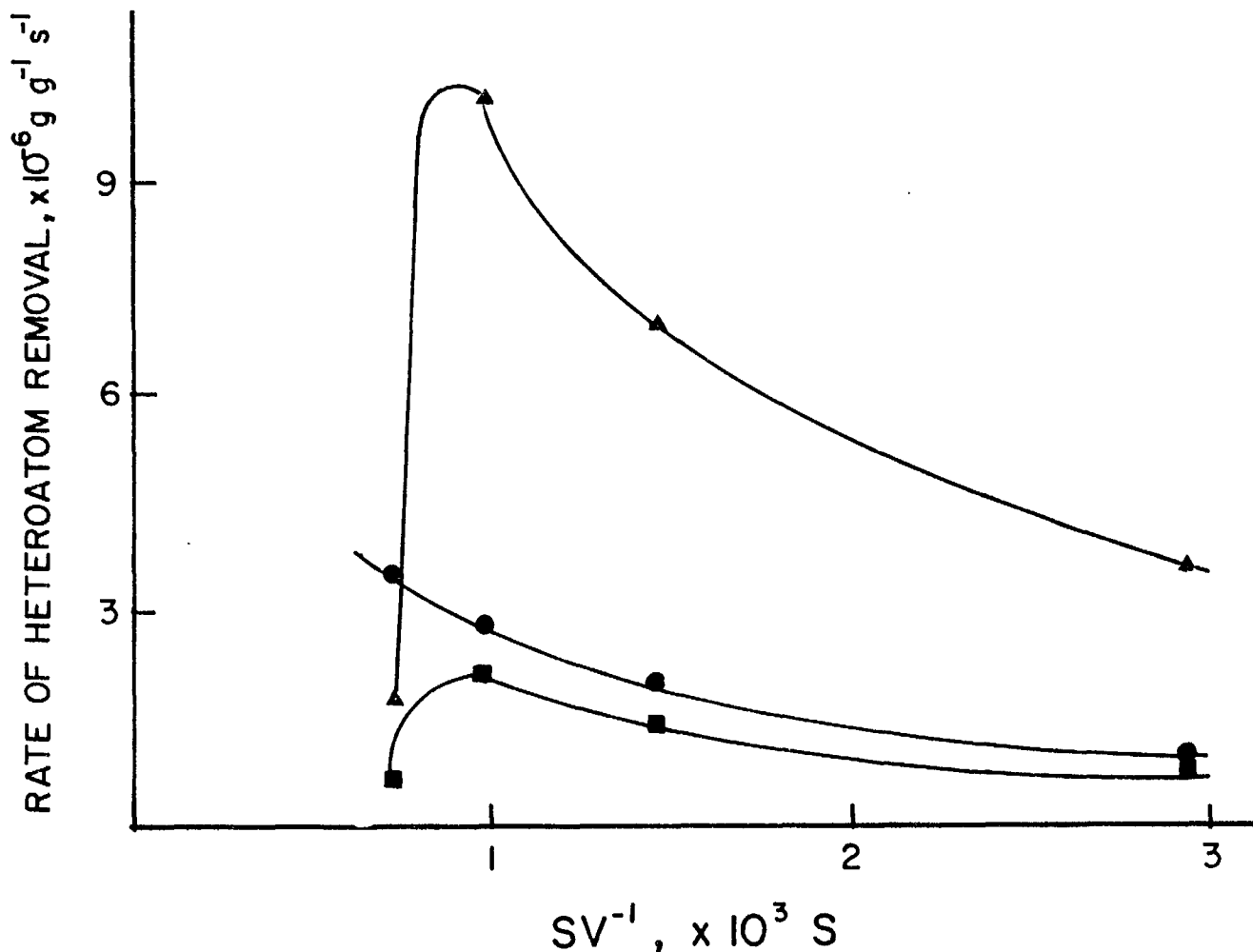
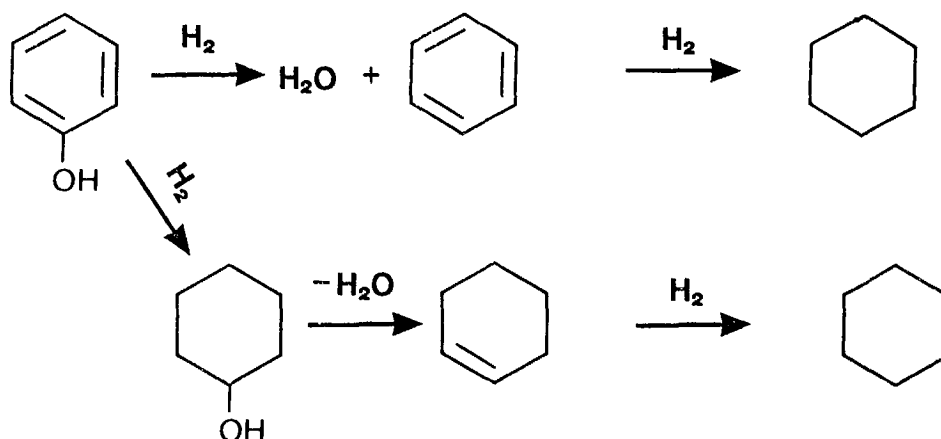


Fig. 4. Effect of residence time (SV<sup>-1</sup>) on sulphur (●), nitrogen (■), and oxygen (▲) removal from coal-derived naphtha at 10.45 MPa and 633 K using Co-Mo/Al<sub>2</sub>O<sub>3</sub>.

The compositional results of capillary gas chromatography (Fig. 5) indicate that the rate of phenol removal parallels the rate of cyclohexane formation. In Fig. 5, the concentrations of phenol, benzene and cyclohexane are plotted against inverse space velocity. Again, the maximum activity occurs at a space velocity corresponding to  $1.25 \times 10^{-3} \text{ g g}^{-1} \text{ s}^{-1}$ . These results suggest the following reaction scheme for phenol removal as described by Odeburmi and Ollis (1983):



The decrease in cyclohexane concentration at the lowest space velocity may be due to isomerization reactions. Otherwise, the total number of moles of phenol, benzene, and cyclohexane is constant for SV from  $3$  to  $14 \times 10^{-4} \text{ g g}^{-1} \text{ s}^{-1}$ ,  $633$  to  $653 \text{ K}$ , and  $10.45$  and  $13.90 \text{ MPa}$ . Studies of gas phase phenol hydrodeoxygenation at atmospheric pressure using the same catalyst indicated complete conversion to benzene only (Fairbridge, 1983b). Neither cyclohexanol nor cyclohexanone were identified in appreciable

quantities. This, however, does not preclude the possibility of aromatic ring hydrogenation as an initial step when higher pressures are employed. Calculations of benzene equilibrium concentrations made by Frost (1933) and reported by Alekseeva and Moldavskii (1959) indicate that the equilibrium conversion of cyclohexane to benzene would not be appreciable under reaction conditions similar to those used in this study. Odeburmi and Ollis (1983) ruled out possible equilibrium shifts in the hydrodeoxygenation of cresols over a similar Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst.

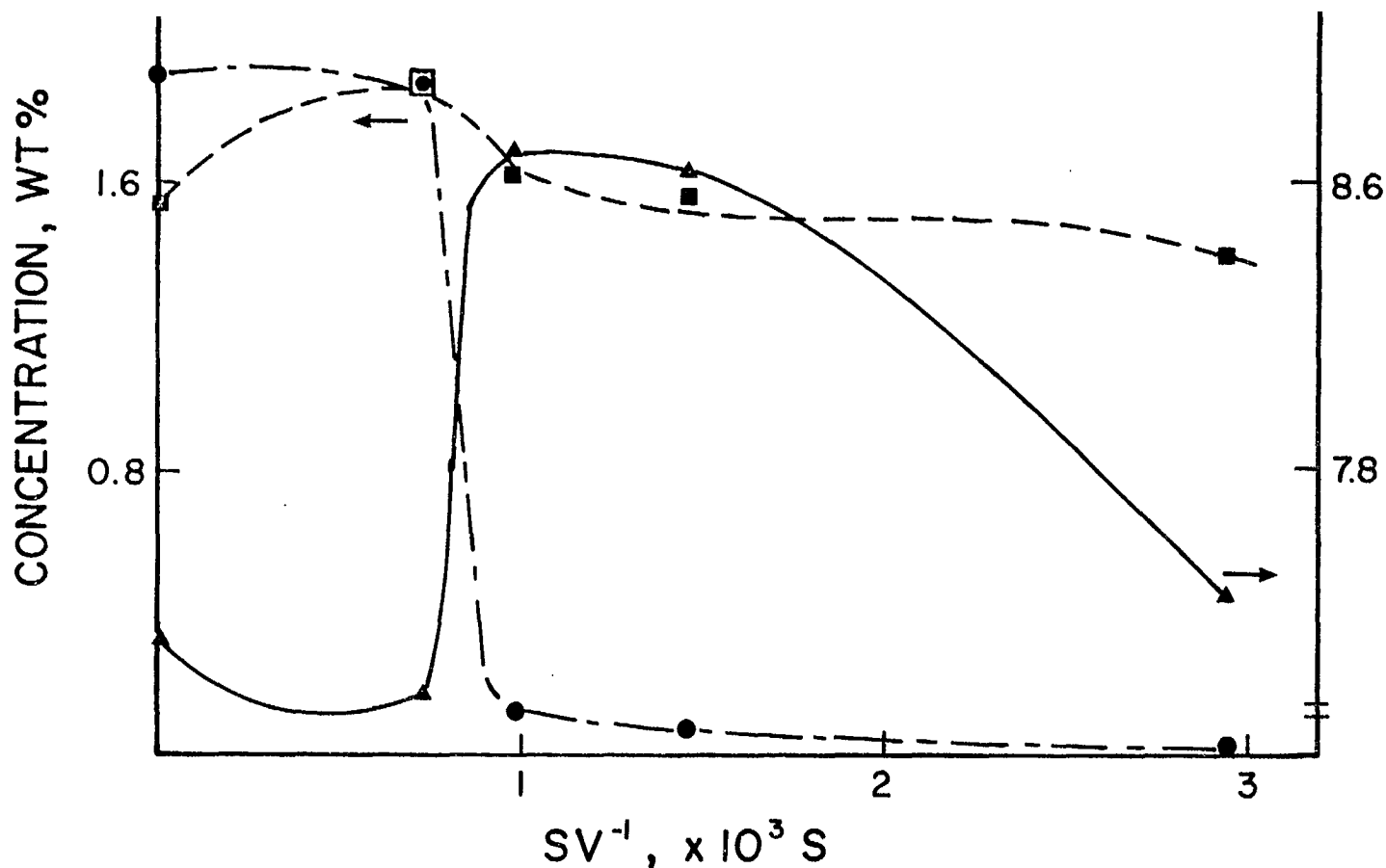


Fig. 5. Effect of residence time ( $SV^{-1}$ ) on phenol (●), benzene (■), and cyclohexane (▲) concentration in coal-derived naphtha hydrotreated at 10.45 MPa and 633 K using Co-Mo/Al<sub>2</sub>O<sub>3</sub>.

The surface area of the catalyst extrudates decreased from 190 to 140 m<sup>2</sup> g<sup>-1</sup> after reaction at 10.45 MPa. The pore volume derived from mercury porosimetry decreased from 0.39 to 0.34 mL g<sup>-1</sup>. Solvent extraction of the used catalyst had little effect on either surface area or pore volume. The loss in pore volume occurred in the 8 to 11 nm diameter range. No serious catalyst deactivation was observed in this study.

Using the data for the conversion of the phenolic compounds at 10.45 MPa, 633 and 653 K, it is also possible to identify a reactivity order for the various phenols. These compounds can be written in order of decreasing reactivity based upon the rate of phenolic compound removal (gram phenol per gram catalyst second) calculated as in equation 3:

phenol > m - cresol > p - cresol > o - cresol >

3,5 - dimethylphenol > 3,4 - dimethylphenol > o - ethylphenol >

2,6 - dimethylphenol

Several studies of the hydrodeoxygenation of phenolic compounds have been reported over similar catalysts (Weigold, 1983; Odeburmi and Ollis, 1983; Elliott, 1983). In addition, there are several reports concerning alkylation (Tanabe and Nishizaki, 1976), dehydration (Karuppannasamy et al., 1980), hydrogenation (Samchenko and Pavlenko, 1980, 1981), and amination (Ono and

Ishida, 1981) of phenolic compounds. Relative reactivity series have often been described using a number of criteria, but direct comparisons among the various studies are difficult because of the different reactor configurations, process conditions and feed compositions.

This study indicated the advantages of catalyst bed dilution for the testing of a commercial catalyst in a bench-scale hydrotreating reactor. Heteroatoms could be effectively removed from a coal-derived naphtha at 13.90 MPa, 673 K, and at a space velocity of  $6.83 \times 10^{-4} \text{ g g}^{-1} \text{ s}^{-1}$  using a commercial Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. Measurements of the experimental rates of heteroatom removal indicated that phenolic oxygen was removed at the fastest rate, followed by sulphur, and then by nitrogen. The rate of sulphur removal was observed to increase with increased space velocity. The rates of oxygen and nitrogen removal increased up to a space velocity of  $1.25 \times 10^{-3} \text{ g g}^{-1} \text{ s}^{-1}$ . At higher SV values, the rates decreased sharply. This unexpected effect of space velocity on heteroatom removal from coal-derived naphtha will be further assessed in future studies.

The results of this work are in agreement with Odeburmi and Ollis (1983) in that the reactivity for hydrodeoxygenation of phenols appears to decrease in the order meta > para > ortho. This appears to hold for both singly and doubly methyl-substituted phenols. Several investigators have indicated the possibility of two adsorbed intermediates - one which leads to direct hydrogenolysis and one which leads to ring hydrogenation followed

by dehydration. The present results indicate that at conditions where phenols are readily converted (633 K and 10.45 MPa), the dual path mechanism is supported in the absence of equilibrium considerations for the conversion of naphthenes to aromatics. The removal of sulphur and nitrogen heteroatoms (99%) requires more severe conditions using a typical commercial Co-Mo/Al<sub>2</sub>O<sub>3</sub> hydrotreating catalyst.

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