COMPETING REACTIONS IN HYDROTREATING COKER DISTILLATES FROM ATHABASCA BITUMEN ON UNPROMOTED AND PROMOTED CATALYSTS

R. Ranganathan, M. Ternan and B.I. Parsons

Energy Research Laboratories
Department of Energy, Mines & Resources
555 Booth Street
Ottawa, Ontario
K1A 0G1

INTRODUCTION

Hydrotreating crude distillates involves competing reactions such as desulphurization, denitrogenation and hydrogenation. Individual studies of these reactions have been described in the literature for several model compounds[1, 2, 3]. In a few cases, the interaction of these competing reactions has been reported[4, 5]. However, it is difficult to simulate all the properties of petroleum using model compounds. It was felt that a study with distillate fractions was required to determine the interaction of these competing reactions in the industrial hydrotreating process. The purpose of the present paper is to describe the interaction of the competing reactions for various catalysts and process conditions as they would be encountered in a refinery application. A coker kerosene distillate, derived from Athabasca bitumen[6], was hydrotreated on unpromoted and promoted catalysts at various reaction temperatures.

EXPERIMENTAL

The catalysts used in this study were unpromoted MoO_3/alumina containing 3, 6, 9 and 12 wt % of MoO_3 and promoted MoO_3/alumina composed of 1.1 wt % CoO - 2.2 wt % MoO_3/alumina, 1.1 wt % NiO - 2.2 wt % MoO_3/alumina and 3 wt % CoO - 12 wt % MoO_3/alumina. The catalysts were prepared by spraying aqueous solutions of metal salts on alumina powder (a mixture of 20 wt % Continental Oil Company "Catapal SB" and 80 wt % "Catapal N" alumina monohydrate) in a mix-muller[7]. The impregnated mixtures were dried in air at 110°C for 3 hours and then calcined at 500°C for 3 hours. The calcined powder was mixed with 2 wt % stearic acid and pressed into cylindrical pellets (L = D = 3.2 mm) in a continuous pelleting press. The pellets were recalcined at 500-550°C for 4 hours to remove the stearic acid. A commercial catalyst, 3 wt % CoO - 12 wt % MoO_3/alumina (Harshaw CoMo 0603T, 3.2 mm pellets), was also used.

The feedstock used for the hydrotreating study was a coker kerosene distillate (193-279°C) supplied by Great Canadian Oil Sands Ltd. of Fort McMurray, Alberta. The properties of the feedstock are listed in Table 1.

The reaction measurements were carried out in a bench scale continuous flow system[8] with the oil and hydrogen flowing up through a fixed bed of catalyst. The reactor was 0.025 m in internal diameter, 0.305 m long, and was made of 316 stainless steel. The reactor was filled sequentially from the bottom with 42 ml of berl saddles, 100 ml of catalyst pellets and 13 ml of berl saddles. The axial temperature profile was measured by a movable thermocouple in a thermocouple well located centrally in the reactor. The gas and liquid reaction products were separated in one of the two down-stream vessels. When steady-state conditions had prevailed for 1 hour, the product flow was routed to the second vessel where the liquid product was collected for subsequent analysis.

For all the experiments the reaction pressure, liquid space velocity and hydrogen flow rate were kept constant at $1.39 \times 10^7 N/m^2$ (2000 psig), $2h^{-1}$ and 890.5 $m^3 H_2/m^3$ oil (5000 scf H_2/bbl oil) respectively. The reaction temperatures were varied in the following sequence: 400, 420, 360, 320 and 400°C. The second run at 400°C was undertaken to check the series and confirm the stability of the catalyst.

The product samples were analysed for sulphur, nitrogen, aromatics, olefins and saturates. The conversions of higher boiling fractions to lower boiling fractions were determined by atmospheric distillation and the sulphur concentration by X-ray fluorescence[9]. The sulphur apparatus was calibrated using a series of oil samples analysed by the bomb sulphur technique[7]. The nitrogen content was measured using a hydrogenation-microcoulometric apparatus developed and manufactured by the Dohrmann Division of Envirotech Corp., Mountain View, California[10]. The Dohrmann procedure was developed for oils containing 10-100 ppm and was calibrated using pyridine, carbazole and acetanilide. The samples having higher nitrogen were diluted to reduce the nitrogen concentration to the working range of the instrument. The aromatics, olefins and saturates were separated using the ASTM standard FIA method[11]. The conversion of fractions boiling above 220°C to fractions boiling below 220°C was calculated using the distillation data in the following equation:

$$X_{BP} = \frac{(100-F) - (100-P)}{100 - F} \qquad (1)$$

where P = wt % of product boiling below 220°C

F = wt % of feed boiling below 220°C

RESULTS AND DISCUSSION

Catalyst Pretreatment:

Preliminary studies showed that the catalyst pretreatment conditions are important in obtaining stable activity[12]. The oxides in the catalysts are slowly converted to sulphides by the hydrogen sulphide produced from the sulphur compounds in the feed. Large variations in catalyst activity have been related to differences in the extent of catalyst sulphiding. It was found that a pretreatment with the coker kerosene feedstock at reaction conditions of $1.39 \times 10^7 N/m^2$ (2000 psig), 673^oK, $2h^{-1}$ and $890.5\ m^3H_2/m^3$ oil (5000 cu ft/bbl) for 2 hours produced an adequate extent of catalyst stabilization.

Kinetics:

Mass transfer effects in catalysts are known to be important, particularly when hydrotreating high boiling petroleum fractions[13]. However, for the system used in this work there were strong indications that mass transfer was not controlling. The fact that the different catalysts had markedly different activities suggests that the effect of external mass transfer was negligible. Other experiments undertaken in this laboratory with a higher boiling gas-oil over extruded catalysts, having different dimensions (0.317 mm and 0.159 mm) but the same chemical composition, also produced the same activity[14]. This indicated that pore diffusional resistance was not controlling. Additional evidence for minimal diffusional effects is obtained when one compares the desulphurization and denitrogenation reaction data of two catalysts having the same metals content (Table 2). For 1.1 wt % NiO - 2.2 wt % MoO_3/alumina, the denitrogenation conversion improved relative to desulphurization conversion with increasing temperature. For 3 wt % MoO_3/alumina, the desulphurization improved relative to denitrogenation conversion with increasing temperature. Such changes indicate that the differences in desulphurization and denitrogenation are not due to pore diffusion effects and can be attributed to kinetics.

The kinetics of denitrogenation, desulphurization and hydrogenation were studied on 3 wt % CoO - 12 wt % MoO_3/alumina catalyst. Denitrogenation followed first order kinetics (Figure 1 A) as reported by others[15]. The desulphurization followed second order kinetics (Figure 1 B).

Similar desulphurization kinetics have been observed by others for high sulphur crudes[16]. However, for low sulphur crudes, first order kinetics have also been reported[13]. Beuther et al[16] and Schuit et al[17] suggest that desulphurization is first order for individual sulphur compounds and appears to be second order in a feedstock containing different types of sulphur compounds.

In the literature, the hydrogenation of aromatics is reported to follow reversible first order kinetics[18]. However, in the work discussed here the data did not fit zero order, first order irreversible, first order reversible or second order irreversible kinetics. This is probably due to the inhibition of the hydrogenation process by sulphur compounds. Voorhoeve and Stuiver[19] reported that the hydrogenation of cyclohexane deviated from first order kinetics when carbon disulphide was present. They suggest that the hydrogenation sites are blocked by the preferential adsorption of CS_2. In the present case it is entirely possible that the sulphur compounds in the feedstock complicated the hydrogenation kinetics in this way.

Effects of Metal Oxide Concentration:

Several catalysts of varying MoO_3 concentration were evaluated. Figure 2 A shows that the % conversion of sulphur increases with MoO_3 concentration and reaches a plateau after 9 wt % MoO_3. The denitrogenation results (Figure 2 B) show similar trends. However, at 320°C the rate of increase of conversion with metal oxide concentration was considerably greater for denitrogenation. At all temperatures studied the denitrogenation conversion is higher than desulphurization for the whole series of unpromoted MoO_3/alumina catalysts. Qader et al[20] also reported that the denitrogenation conversion was higher than desulphurization conversion for low temperature distillate from coal tar (200 - 325°C, 0.83 wt % S and 0.40 wt % N) on a WS_2 catalyst at pressures above 1000 psig. However, Williams et al[21] found that desulphurization conversions were greater than denitrogenation conversions for a heavy gas-oil (345 - 525°C, 3.59 wt % S and 0.38 wt % N) on unpromoted MoO_3/alumina catalysts at 2000 psig. The combined results indicate that the nitrogen in the heavier fractions is much more difficult to remove.

Hydrogenation of aromatics in coker kerosene distillate showed a trend different from denitrogenation and desulphurization (Figure 2 C). A 3 wt % MoO_3/alumina catalyst showed significantly higher hydrogenation conversion than the pure alumina support. However, further increases in MoO_3

concentration only slightly improved the hydrogenation of aromatics.

The conversion of fractions boiling above 220°C to fractions boiling below 220°C (equation 1) was measured for all catalysts studied. At 400°C, the per cent conversion increased with increasing metal oxide concentration up to 9 wt % MoO_3 and decreased above 9 wt % (Figure 2 D). At 320°C, the maximum was at 6 wt % MoO_3. The findings of Seshadri et al[22] may provide a partial explanation for the maximum in conversion. They found that, for MoO_3/alumina catalysts, the catalytic activity in vapour-phase aldol condensation of n-butyraldehyde and the esr signals (indicating Mo^{5+} concn.) showed maxima at 9 wt % in MoO_3, suggesting that Mo^{5+} centers may be responsible for molecular weight reduction. Desulphurization, denitrogenation and hydrogenation conversions did not show these maxima. It would appear that quite different sites are involved for molecular weight reduction than for the refining reactions.

Effects of Promoters:

At low reaction temperatures the addition of promoters to MoO_3/alumina catalysts affected the desulphurization, denitrogenation and hydrogenation processes differently. Comparing catalysts containing 2.2 wt % MoO_3/alumina and 1.1 wt % CoO - 2.2 wt % MoO_3/alumina, the conversions at 320°C for desulphurization, denitrogenation and aromatic hydrogenation increased from 20 to 76.7%, 30 to 48% and 31 to 43% respectively (Figures 1 A, 1 B and 1 C and Table 2). A laboratory catalyst containing 12 wt % MoO_3/alumina was compared with a commercial catalyst having 3 wt % CoO - 12 wt % MoO_3/alumina. In this case the conversions improved from 38.8 to 93.5%, 57.2 to 79.3% and 40.5 to 49.2% respectively. The promotion of MoO_3/alumina with nickel showed similar increases in desulphurization, denitrogenation and hydrogenation (Table 2). At 320°C the increase in conversions due to promoter addition varied in the following order:

desulphurization > denitrogenation > aromatic hydrogenation

The results show that the addition of cobalt or nickel to molybdenum/alumina significantly increases the selectivity for the desulphurization reaction in particular. The promoter would appear to change the chemisorption characteristics of sulphur compounds in such a way as to selectively improve desulphurization.

Similar results were obtained by Williams et al[21] showing that the addition of a promoter selectively increased the desulphurization conversion. They found that, at 380°C for 3 wt % CoO - 12 wt % MoO_3 catalysts, the desulphurization and denitrogenation conversions were 78% and 24% respectively compared to 35% and 16% for 12 wt % MoO_3 catalysts. The important point to note is that the different types of compounds present in the low boiling coker kerosene and the heavy gas-oil feedstocks did not affect the promotion of desulphurization by cobalt or nickel.

Comparison of Denitrogenation and Desulphurization at Different Temperatures:

The rate constants calculated using the first order equations for denitrogenation and the second order equations for desulphurization are shown in Arrhenius plots (Figures 3 & 4). The results obtained for both promoted and unpromoted catalysts are given. It is seen from Figure 3 that the activation energies (proportional to the slopes of the lines) for denitrogenation decrease with increasing concentrations of unpromoted MoO_3 on alumina. On the other hand, for desulphurization (Figure 4) the activation energies increase with increasing MoO_3 concentration. Cremer[23] suggests that one of the reasons for variations in activation energies and frequency factors is the difference in the strength of adsorption. In the present work, the variations in activation energies also suggest that the differences in denitrogenation and desulphurization conversions on MoO_3/alumina are caused by differences in strengths of chemisorption of sulphur and nitrogen compounds on the catalyst. When Ni or Co promoter was added the activation energies for both denitrogenation and desulphurization decreased, but there was a large increase in the frequency factor for the desulphurization reaction compared to the denitrogenation reaction.

Satterfield et al[4] suggest that the interaction between desulphurization and denitrogenation is temperature-dependent. They studied the desulphurization of model compounds such as thiophene and the denitrogenation of pyridine on commercial CoMo, NiMo and NiW sulphided catalysts at temperatures up to 425°C and pressures up to 1.1×10^3 kN/m^2 (11 atm). At low temperatures, thiophene inhibited denitrogenation and at high temperatures the sulphur compounds enhanced the denitrogenation. The results obtained with distillate fractions and the promoted catalysts both in the present work and by Williams et al[21] support the observations of Satterfield et al[4]. With the coker distillate over Co and Ni promoted catalysts, the desulphurization was much

higher than denitrogenation at 320°C, but the denitrogenation conversion improved relative to desulphurization with increasing temperature (Table 2). Also, Williams et al found that for similar promoted MoO_3/alumina catalysts (Table 3), the differences between the conversions for denitrogenation and desulphurization decreased at higher reaction temperatures.

With the unpromoted catalysts, on the other hand, the hydrotreating data shows a reverse trend. The results for the unpromoted catalysts (Figures 1 A, 1 B and Table 2) with the coker distillate and of Williams et al on gas-oil (Table 3) show that with increasing reaction temperature, the desulphurization reaction conversion improves relative to denitrogenation conversion. A comparison of relative conversions for desulphurization and denitrogenation at different temperatures definitely indicates that the interaction of these reactions depends on whether the catalyst is promoted or not.

CONCLUSIONS

Comparison of molecular weight reduction and the refining reactions on unpromoted MoO_3 catalysts indicates that quite different active sites are involved for molecular weight reduction than for the refining reactions. Variations in trends for apparent activation energies of desulphurization and denitrogenation on unpromoted catalysts indicate differences in chemisorption characteristics of nitrogen and sulphur compounds.

With the promoted catalysts, the kinetics observed with the distillate fractions generally agrees with the results of the pure compound studies. The trend of the data was the same regardless of the boiling range of the distillate. However, in the case of unpromoted catalysts, the boiling range of the feedstock has a considerable influence on the reaction rates. Comparison of the high pressure data for coker kerosene reported here, the high pressure data of Williams et al[21] and the low pressure data reported by Satterfield et al[4] indicates that with increasing reaction temperature, the presence of sulphur compounds enhances denitrogenation relative to desulphurization on promoted catalysts but not on unpromoted catalysts.

ACKNOWLEDGEMENTS

The authors wish to thank R.G. Draper, E. Kowalchuk, G.R. Lett, S. Soutar, E. McColgan, R.J. Williams and R.W. Taylor for their technical assistance.

REFERENCES

1. Amberg, C.H. and Owens, P.J., Advances in Chemistry Series 33, 182 (1961)

2. Doleman, J. and Vlugter, J.C., Proceedings of Sixth World Petroleum Congress, Frankfurt, West Germany, Section 111, 247 (1964)

3. Voorhoeve, R.J.H., J. Catalysis 23, 236 (1971)

4. Satterfield, C.N., Modell, M. and Mayer, J.F., A.I.Ch.E. Journal, 21 (6), 1100 (1975)

5. Rosenheimer, M.O. and Kiovsky, J.R., ACS Preprints (Petroleum) Chicago Meeting, Sept. 11, 1967, p B-147

6. Bachman, W.A. and Stormont, D.H., Oil and Gas J., 65 (43), 69 (1967)

7. Williams, R.J., Draper, R.G. and Parsons, B.I., Technical Bulletin TB 187, Department of Energy, Mines & Resources, Ottawa, Canada (1973)

8. Takematsu, T., and Parsons, B.I., Technical Bulletin TB-161, Dept. of Energy, Mines & Resources, Ottawa, Canada (1972)

9. Frechette, G., Herbert, J.C., Thinh, T.P. and Miron, T.A., Hydrocarbon Processing, 54 (2), 109 (1975)

10. Fabbro, L.A., Filachek, L.A., Iannacone, R.L., Moore, R.T., Joyce, R.J., Takahashi, Y. and Riddle, M.E., Anal. Chem. 43, 1671 (1971)

11. ASTM Method D-1319

12. Ranganathan, R., Ternan, M., and Parsons, B.I. - publication in "Fuel" (in preparation)

13. Schuman, S.C. and Shalit, S.C., Catalysis Reviews 4 (2), 245 (1970)

14. Whalley, M. and Ternan, M. - unpublished results

15. Flinn, R.A., Larson, O.A. and Beuther, H., Hydrocarbon Processing 42 (9), 129 (1963)

16. Beuther, H. and Schmid, B.K., Proc. 6th World Petroleum Cong., Frankfurt, 3, 297 (1963)

17. Schuit, G.C.A. and Gates, B.C., A.I.Ch.E. Journal 19 (3), 417 (1973)

18. Gully, A.J. and Ballard, W.D., Adv. in Pet. Chem. and Ref. 7, 240 (1963)

19. Voorhoeve, R.J.H. and Stuiver, J.C.M., J. Catalysis 23, 228 (1971)

20. Qader, S.A., Wiser, W.H. and Hill, G.R., Ind. and Eng. Chem. Proc. Des & Dev. 7 (3), 390 (1968)

21. Williams, R.J., Ternan, M. and Parsons, B.I., Report ERP/ERL 75-85 (R), Energy Research Laboratories, Dept. of Energy, Mines and Resources, Ottawa, Canada (1975)

22. Seshadri, K.S. and Petrakis, L., J. Phys. Chem. 74, 4102 (1970)

23. Cremer, E., Advances in Catalysis 7, 83 (1955)

TABLE 1

PROPERTIES OF THE FEEDSTOCK

Properties		Coker Kerosene Distillate
Boiling range,	^{o}C	193 - 279
Specific Gravity 60/60	^{o}F	0.871
Sulphur,	wt %	2.32
Nitrogen,	ppm	430
Pour Point,	^{o}F	Below -60
Cloud Point,	^{o}F	Below -60
Flash Point,	^{o}F	116
Vanadium,	ppm	0.40
Nickel,	ppm	0.36
Iron,	ppm	0.50
Ramsbottom Carbon Residue (10% bottoms),	wt %	0.29
Aromatics + olefins,	vol %	58
Saturates,	vol %	42

TABLE 2

DESULPHURIZATION, DENITROGENATION AND HYDROGENATION OF COKER KEROSENE ON PROMOTED AND UNPROMOTED CATALYSTS

Catalysts	*Promoted*								*Unpromoted*			
Concn metal oxides	1.1 wt % CoO-2.2 wt % MoO_3/alumina				1.1 wt % NiO-2.2 wt % MoO_3/alumina				3 wt % MoO_3/alumina			
Reaction temperature, °C	320	360	400	420	320	360	400	420	320	360	400	420
% desulphurization	76.7	92.7	96.6	96.6	71.1	94.0	96.1	96.1	26.7	56.5	87.1	92.2
% denitrogenation	48.1	82.3	95.3	97.7	50.9	86.1	96.3	98.6	34.4	68.6	91.2	94.0
% hydrogenation	43.2	54.1	56.6	56.8	42.9	52.2	55.8	57.5	34.9	43.4	55.3	56.3

TABLE 3

GAS OIL HYDROTREATING ON
PROMOTED AND UNPROMOTED CATALYSTS
Williams et al (21)

Catalyst	Promoted		Unpromoted							
Concn metal oxides	3 wt % CoO - 12 wt % MoO_3		3 wt % MoO_3		6 wt % MoO_3		9 wt % MoO_3		12 wt % MoO_3	
Reaction temperature, ^{o}C	380	450	380	450	380	450	380	450	380	450
% desulphurization	78	93	26	74	29	81	36	87	35	85
% denitrogenation	24	73	0	24	0	45	8	61	16	63

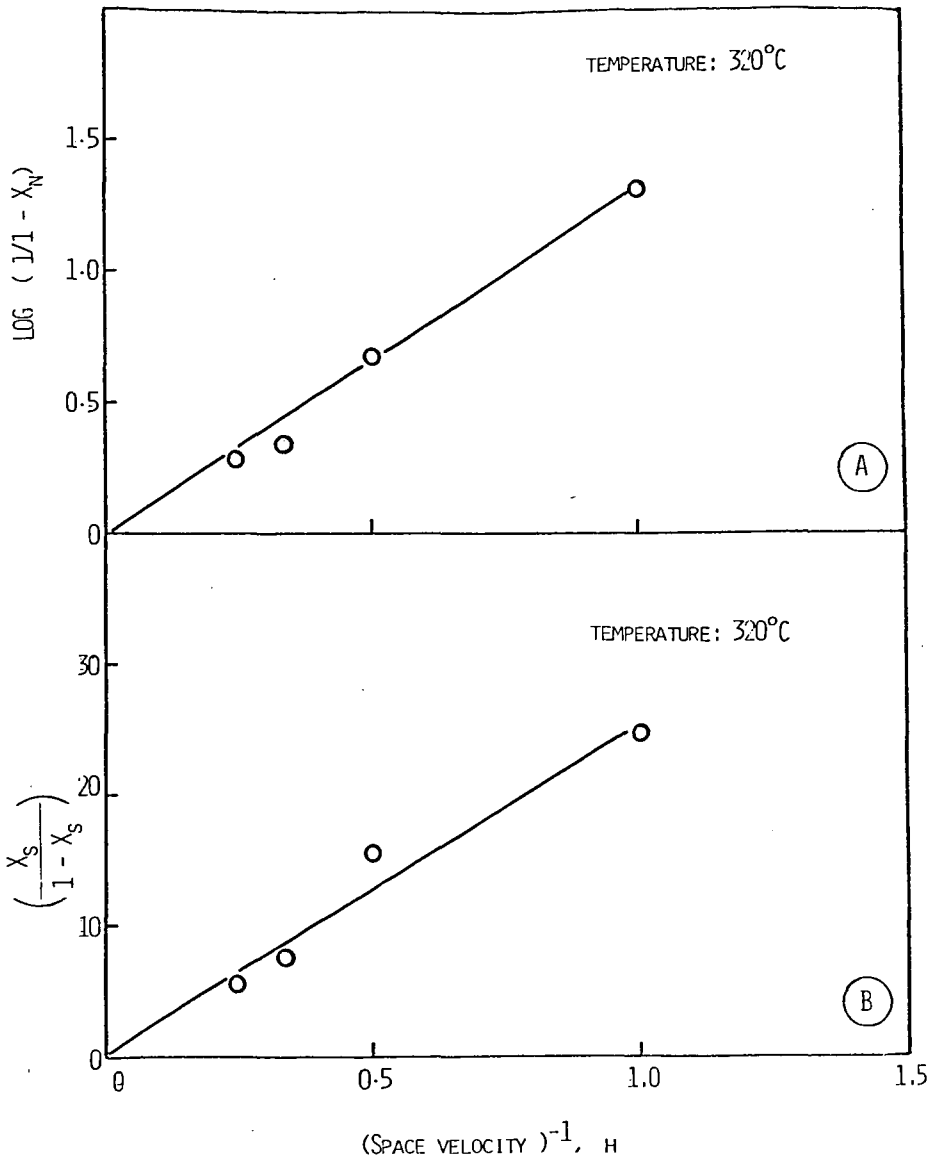

FIGURE 1 A FIRST ORDER PLOT FOR DENITROGENATION (X_N - FRACTIONAL NITROGEN CONVERSION)

FIGURE 1 B SECOND ORDER PLOT FOR DESULPHURIZATION (X_S - FRACTIONAL SULPHUR CONVERSION)

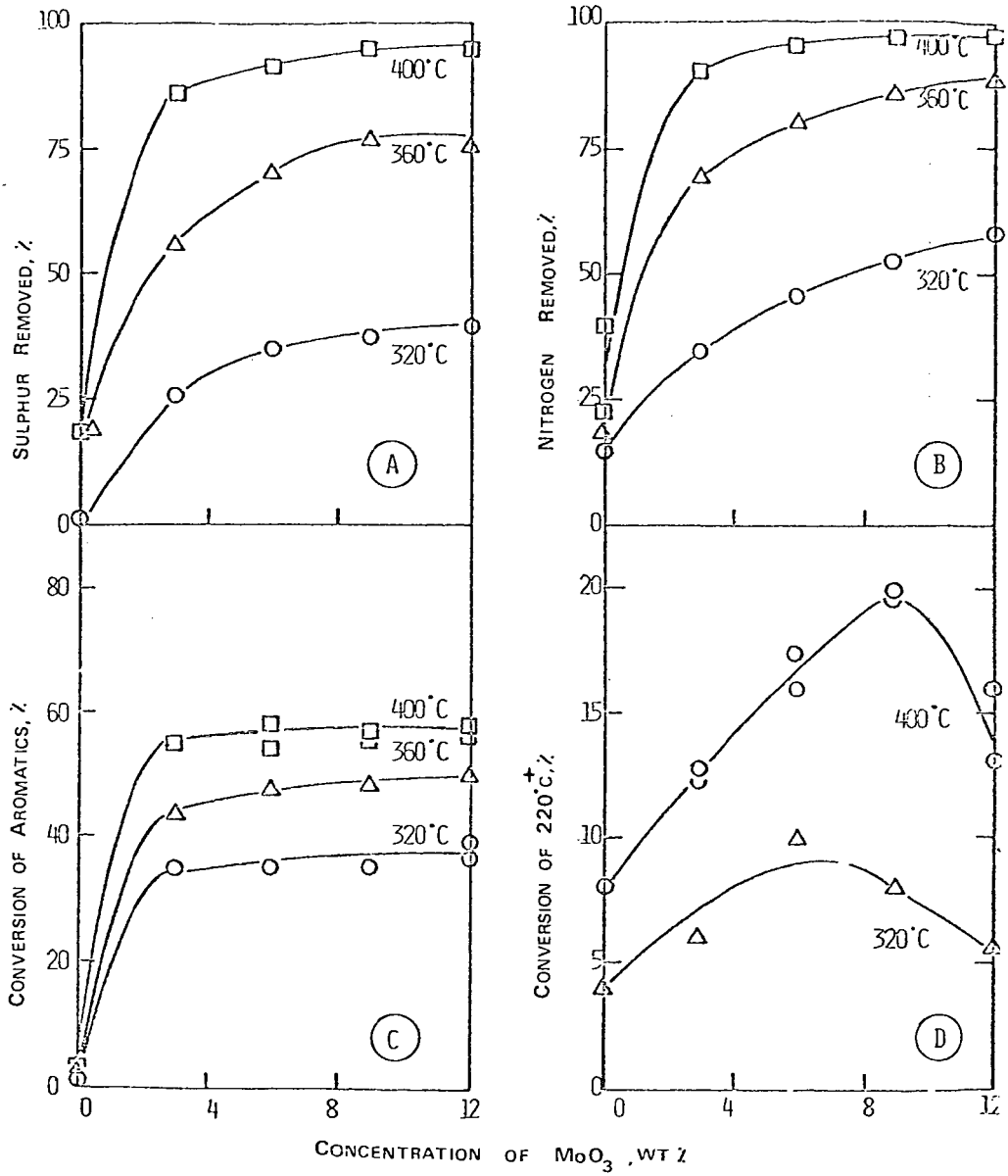

FIGURE 2 - EFFECT OF METAL OXIDE CONCENTRATION ON: A - DESULPHURIZATION CONVERSION
B - DENITROGENATION CONVERSION
C - HYDROGENATION OF AROMATICS
D - CONVERSION OF FRACTIONS BOILING ABOVE 220°C

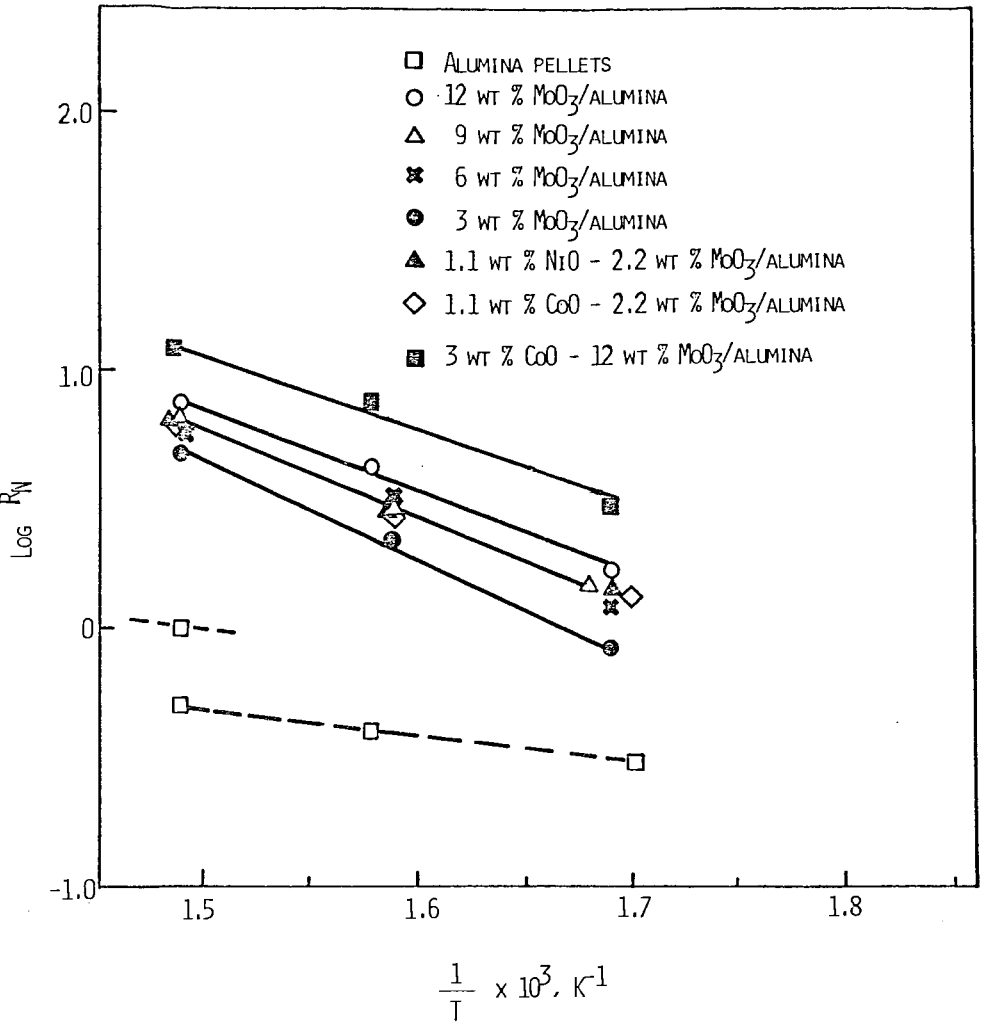

FIGURE 3 - ARRHENIUS PLOT FOR DENITROGENATION
(k_N - FIRST ORDER RATE CONSTANT)

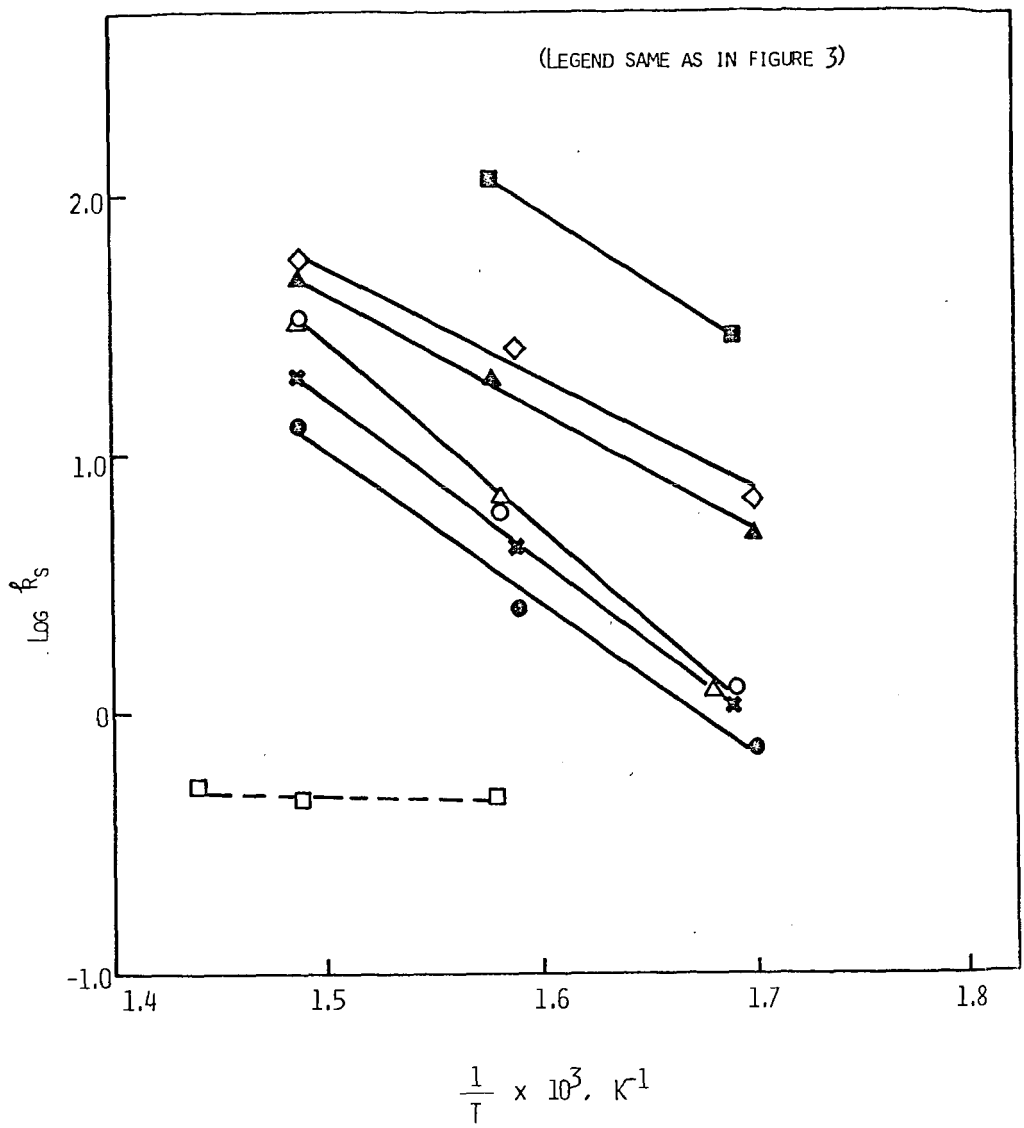

FIGURE 4 - ARRHENIUS PLOT OF DESULPHURIZATION
(k_S - SECOND ORDER RATE CONSTANT)