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UPGRADING OF MIDDLE DISTILLATE FRACTIONS
OF A SYNCRUDE FROM ATHABASCA OIL SANDS

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UPGRADING OF MIDDLE DISTILLATE FRACTIONS OF A
SYNCRUDE FROM ATHABASCA OIL SANDS

by

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ABSTRACT

Current processes for upgrading bitumen from Athabasca oil sands produce synthetic crudes which are high in aromatics and deficient in hydrogen. As a consequence, middle distillate fractions derived from these syncrudes produce diesel fuels of low cetane number and jet fuels which are hydrogen deficient. Results obtained from bench-scale hydrotreating experiments indicate that quality fuels may be produced from Athabasca syncrudes. Middle distillate fractions from this source were subjected to high severity hydroprocessing in a continuous-flow reactor unit using conventional hydrotreating catalysts which were pre-sulphided by a mixture of H_2/H_2S . Aromatic hydrogenation at high temperatures and pressures was affected by the approach to thermodynamic equilibrium, however, at lower temperatures, in some cases virtually 100 percent saturation was achieved and treated fractions were found to meet cetane number and jet fuel smoke point requirements. Data treatment in the present study includes a model for the hydrogenation kinetics and correlations between aromatic carbon content and fuel combustion properties.

VALORISATION DES FRACTIONS DE DISTILLATS MOYENS D'UN
BRUT SYNTHÉTIQUE PROVENANT DES SABLES BITUMINEUX
D'ATHABASCA

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RÉSUMÉ

Les procédés courants de valorisation du bitume extrait des sables bitumineux d'Athabasca permettent d'obtenir des bruts synthétiques ayant une teneur élevée en composés aromatiques et faible en hydrogène. En conséquence, les fractions de distillats moyens dérivés de ces bruts synthétiques produisent des combustibles diesel ayant un faible indice de cétane et une déficience en hydrogène. Les résultats obtenus à partir d'expériences d'hydrotraitement réalisées en laboratoire indiquent que des combustibles de bonne qualité peuvent être produits à partir des bruts synthétiques d'Athabasca. Les fractions de distillats moyens tirés de cette source ont été soumises à un traitement par l'hydrogène très poussé dans un réacteur à écoulement continu en utilisant des catalyseurs d'hydrotraitement classiques qui avaient été pré-sulfurés au moyen d'un mélange de H_2 et de H_2S . La quasi-réalisation de l'équilibre thermodynamique à des températures et des pressions élevées a influé sur l'hydrogénation des aromatiques, cependant, à des températures inférieures, il a été constaté que dans certains cas la saturation avait presque atteint 100 p. 100 et que les fractions traitées répondaient aux exigences relatives à l'indice de cétane et au point de fumée des carburateurs. Dans la présente étude, le traitement des données comprend l'établissement d'un modèle cinétique de l'hydrogénation, ainsi que l'établissement de corrélations entre la teneur en carbone des aromatiques et les propriétés de combustion des combustibles.

INTRODUCTION

Synthetic crude oil is presently produced in Canada from two commercial operations which process bitumen from Athabasca oil sands in northern Alberta. In both plants the synthetic crude is produced by upgrading the bitumen through coking processes and further refining by severe hydrotreating.

The hydrotreating removes sulphur, nitrogen, and also hydrogenates olefins and some aromatics. The extent of aromatic saturation is a function of the process severity. Much of the middle distillate produced from Athabasca oil sand syncrudes remains highly aromatic. Diesel fuels which are produced from highly aromatic feedstocks have poor ignition qualities and jet fuels from these sources cause overheating in turbo engines resulting in increased maintenance costs.

Blending of synthetic with conventional crudes is the current practice for accommodating unconventional feedstocks in refinery operations. The amount blended is a function of the total product slate. Canadian refineries are usually limited to a synthetic crude intake of between 20-30% and middle distillate fuels are usually the limiting factor.

Additional hydroprocessing of the synthetic distillates may be an acceptable alternative for producing quality fuels. Adding hydrogen to saturate aromatics in conventional distillates and converting them to naphthenes has been practiced by refineries for some time. It is important to note that although saturation of aromatics may improve the hydrogen/carbon ratio of synthetic distillates, the disproportion of paraffins

in these fuel sources is a fundamental problem. Increasing the naphthene content by conversion of aromatics may only marginally improve the combustion properties of a fuel. For example, the aromatic content of the feedstock used in this study was reduced significantly by severe hydro-treating (which followed delayed coking in the commercial process) but the product still did not meet the Canadian cetane number specification for diesel fuel.

This study was carried out to investigate effects of additional hydroprocessing on the product quality, particularly its diesel ignition and smoke point properties. The aim was to establish the extent of conversion required to enhance the fuel combustion quality and also to correlate cetane ratings and smoke point values for various fuels with their aromatic content. It was also necessary to evaluate the activity of the hydrotreating catalysts since the literature contains little work on catalyst selection for saturating aromatics in this type of feedstock. The catalyst activity was compared by elucidating the reaction kinetics. Finally, it was necessary to investigate the effect of the thermodynamic equilibrium on the aromatic saturation process and to establish the optimum operating conditions to be used as a basis for future work.

EXPERIMENTAL

The feedstock was a middle distillate fraction cut from a synthetic crude oil produced by delayed coking of Athabasca bitumen. The properties of the feedstock are given in Table 1. Three different commercial catalysts were used for hydroprocessing the feed; these were typical hydrotreating catalysts, i.e. $\text{CoO-MoO}_3/\gamma\text{-Al}_2\text{O}_3$, $\text{NiO-MoO}_3/\gamma\text{-Al}_2\text{O}_3$ and $\text{NiO-WO}_3/\gamma\text{-Al}_2\text{O}_3$. The properties of the catalysts are presented in Table 2.

A detailed description of the hydrotreating system has been published previously (1). Experimental runs were carried out using a bench-scale continuous flow reactor operating in the up-flow mode. Liquid feed and hydrogen were mixed, passed through a pre-heater and then over a fixed bed of catalyst in a 316 stainless steel 0.305 x 0.025 m i.d. tubular reactor having a total capacity of 155 cm³. The reactor furnace consisted of three separate heating zones. The heat input to each zone was controlled to maintain the catalyst bed at a constant isothermal temperature. The axial temperature profile was measured by a movable thermocouple located in a thermo-well mounted centrally in the reactor. For each experimental run the reactor was filled sequentially from the bottom with 42 cm³ of berl saddles, 100 cm³ of catalyst extrudates or spheres and 13 cm³ of berl saddles.

The catalyst was sulphided at 380°C and atmospheric pressure by passing a mixture of 10% H₂S in hydrogen over the bed for 2 hours. The volume of H₂S passed was equivalent to eight times the amount of sulphur required for the formation of sulphides. Immediately after sulphiding, the reactor was pressurized with hydrogen ready for the first run. The unit was run for 8 hours on oil before the first steady-state sample was taken. The catalyst loadings to the reactor were 70 grams for the Co-Mo/Al₂O₃ and Ni-W/Al₂O₃ catalysts and 81 grams for the Ni-Mo/Al₂O₃ catalyst respectively (these amounts were required for 100 cm³ of reactor volume).

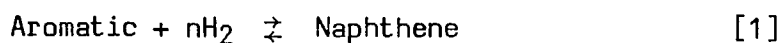
For most of the experimental runs the reactor pressure was maintained at 17.3 MPa (2500 psig). (This condition was chosen because the feedstock was previously hydrotreated in primary upgrading at 10.4 MPa (1500 psig) over a sulphided Ni-Mo/Al₂O₃ catalyst). To investigate the effect on the thermodynamic equilibrium reaction the pressure was also varied in the range 7.00-17.3 MPa. Experimental runs were performed at temperatures of 340-440°C, liquid space velocities of 0.75-2.25 h⁻¹ and a hydrogen flow rate of 530 l (hydrogen) l⁻¹ (feedstock) (3000 scf/bbl). The reactor system was maintained at steady-state conditions for 1 h prior to and 2 h during the period in which product was collected. The hydrotreated product was analyzed for aromatic carbon content by C¹³ NMR analysis using a Varian XL-200 spectrometer. Sulphur content was analyzed by the Wickbold technique and carbon, hydrogen and nitrogen analysis was carried out using a Perkin Elmer 240B analyzer. The average molecular weight of the feedstock was determined with a Knauer vapour pressure osmometer. The catalyst total pore volume was determined with a Micromeritics Model 910 mercury porosimeter. The mean reactor residence time for aromatic saturation was calculated from a knowledge of the total voidage of the catalyst bed, the hydrogen flow rate and the average molecular weight of the feed. Complete vaporization of feed on contacting the catalyst bed was assumed.

Based on operating conditions determined from the work on reaction kinetics, samples of fuel were generated by continuous processing and tested to evaluate their combustion quality. Cetane numbers were determined using a standard CFR test engine. A standard smoke point test (one of the jet fuel quality indicators) was also performed.

RESULTS AND DISCUSSION

Effect of Thermodynamic Equilibrium on Aromatic Saturation

A high degree of aromatic saturation of a middle-distillate may be achieved using a single-stage hydrotreating unit operating under severe process conditions. However, the conversion to naphthenes is a reversible reaction and involves a chemical equilibrium which is temperature dependent:



At high temperatures the extent of conversion may therefore be limited by the approach to thermodynamic equilibrium. Because of this limiting factor it is important to find the optimum operating conditions.

Since aromatic compounds generally have higher relative densities than their corresponding naphthenes we expect the relative density to decrease with the extent of conversion. Figure 1 shows a plot of the relative density of hydrotreated distillate as a function of LHSV for each reaction temperature using the sulphided cobalt-molybdenum and nickel-tungsten catalysts. It is found that the values show a steady decrease with reaction temperature, the effect being greater for the cobalt-molybdenum catalyst. Thus, with increase in temperature the values do not pass through a minimum as would be expected from other experimental evidence shown in the following text. It should be mentioned at this point, however, that aromatic hydrogenation may be accompanied or followed by cracking reactions such as ring opening or chain fragmentation. Reduction of the overall molecular weight would naturally be indicated by lower densities. The cracking reactions are known to be

enhanced with increasing temperatures. We are therefore led to believe that the decrease in relative density at the higher temperatures (400-440°C) is caused by reactions other than aromatic saturation such as cracking of the distillate to lighter products.

Figures 2 and 3 show the effect of change of LHSV on the % aromatic carbon in the hydrotreated product using the nickel-tungsten and cobalt-molybdenum catalysts respectively over the complete temperature range. For both catalysts all curves show a minimum within a temperature range of 380-400°C. Above this temperature the effect of thermodynamic equilibrium is observed as the aromatic carbon content begins to increase again. The plots also show that at any operating condition the extent of aromatic conversion was significantly greater using the nickel-tungsten catalyst. At a pressure of 17.3 MPa, the maximum conversion was achieved at 380°C and 0.75 LHSV. Under these conditions the aromatic carbon content was reduced to 0.41% corresponding to a 97% conversion.

Although very good reproducibility for the data in Figures 2 and 3 has been confirmed, a simple explanation for all the patterns is not apparent. For instance, the curves in the equilibrium domain (high temperature end) should be converging together at the same aromaticity level for both catalysts, but a spread in the aromatic carbon content of 1-2% is evident. The consistently higher product aromaticity when using the Co-Mo catalyst (even near equilibrium) suggests some differences in aromatic-type distributions resulting from the use of the two different catalysts.

Figure 4 shows the effect of hydrogen partial pressure change on the conversion of aromatic carbon in the feedstock over sulphided nickel-tungsten catalyst. The results cover the complete temperature range for a constant liquid hourly space velocity of 1.00. It is

observed that over the pressure range 7.00-17.3 MPa the degree of aromatic carbon conversion is reduced significantly. Each curve demonstrates the effect of the equilibrium condition versus saturation kinetics, the minimum being shifted to the left with decreasing hydrogen pressure. It is also to be noted that at a temperature of 440°C and pressure of 7.00 MPa the equilibrium percent aromatic carbon is 15.9 and greater than that of the feedstock. It is apparent that the data revealed by these plots have importance in determining the optimum operating conditions needed to produce fuels which meet the required combustion standards. The implications of these operating conditions on fuel quality is discussed in the final part of this report.

Kinetics of Aromatic Saturation

The equilibrium reaction given by equation [1] is the basis for elucidating the reaction kinetics. Two simplifying assumptions are also made:

- (i) the forward reaction is assumed to be pseudo-first-order since the hydrogenation is carried out in large hydrogen excess at constant partial pressure
- (ii) the reverse reaction is also assumed to be first-order in naphthene carbon.

The aromaticity of the feedstock is defined as the percentage of aromatic carbon (% C_A) as determined by C^{13} NMR. The fraction of carbon atoms which are aromatic is therefore given by $A = \% C_A/100$. Similarly the fraction of naphthene carbon atoms is given by $N = \% C_N/100$. The rate expression for the reversible reaction is then given by:

$$\frac{-dA}{dt} = k_1 A (P_{H_2})^n - k_1' N \quad [2]$$

where k_1 and k_1' are the forward and reverse rate constants and P_{H_2} is the hydrogen partial pressure.

Introducing assumption (i) equation [2] becomes:

$$\frac{-dA}{dt} = k_f A - k_1' N \quad [3]$$

where $k_f = k_1 (P_{H_2})^n = \text{constant}$.

At equilibrium the forward and reverse reaction rates are equal and therefore:

$$\frac{k_f}{k_1'} = \frac{N_e}{A_e} \quad [4]$$

Also, by a simple mass balance:

$$A + N = A_e + N_e \quad [5]$$

where A_e and N_e are the equilibrium fractions of aromatic and naphthene carbons respectively. Using equations [3], [4] and [5] it follows that:

$$\frac{-dA}{dt} = k_f (1 + A_e/N_e) (A - A_e) \quad [6]$$

Putting $k_R = k_f (1 + A_e/N_e)$ and integrating, we obtain the final expression:

$$\ln \frac{A - A_e}{A_0 - A_e} = -k_R t \quad [7]$$

where A_0 is the initial aromatic concentration. The equilibrium aromatic fractions were estimated from the literature data of Wilson et al (2) and Frye (3).

Figure 5 compares pseudo-first-order-reversible rate plots for the sulphided cobalt-molybdenum and nickel-molybdenum on alumina catalysts over the temperature range 340-400°C. A good fit to the kinetic data found gives support to the assumptions made in developing the rate expression. Figure 5 also shows that the sulphided nickel-molybdenum catalyst has a higher activity than cobalt-molybdenum for hydrotreating the feedstock. Figure 6 shows a similar plot for the sulphided nickel-tungsten catalyst again indicating the superior activity of this catalyst in comparison with the molybdenum catalysts. For example, at any given temperature the reaction rates for the nickel-tungsten catalyst were found on average to be greater than those of cobalt-molybdenum by a factor of two.

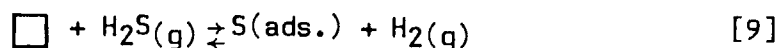
The pseudo-rate-constants, k_R , were determined from the kinetic data by regression-analysis and used in the Arrhenius equation:

$$\ln k_R = \ln A - E/RT \quad [8]$$

where, A is the Arrhenius pre-exponential factor, E the activation energy and R the gas constant. Arrhenius plots for the three catalysts used are presented in Figure 7. Regression-analysis on the data gave values of activation energies and pre-exponential factors which are shown in Table 3. The activation energies 63 and 60 kJ mol⁻¹ for the sulphided cobalt-molybdenum and nickel-tungsten catalysts agree within experimental error but the corresponding value of 83 kJ mol⁻¹ for the nickel-molybdenum catalyst is significantly higher. All of the activation energies compare reasonably well with the value of 71 kJ mol⁻¹ obtained by Voorhoeve and Stuiver for benzene hydrogenation over sulphided nickel-tungsten on alumina at 300-400°C (4). Figure 7 also reveals that the activity of the

nickel-molybdenum catalyst approaches that of nickel-tungsten at the higher temperatures.

The previous studies of hydrogenation kinetics using nickel-tungsten catalysts carried out by Voorhoeve and Stuiver demonstrated that the hydrogenation sites can be blocked by hydrogen sulphide (4). In the present study low concentrations of the gas were liberated during hydrodesulphurization. It is concluded that the sulphur content of the feedstock has an adverse effect on the reaction rate and it is the number of active sites on the catalyst surface that is affected by H₂S and not their intrinsic activity. It is widely accepted that the active sites in these catalysts are caused by anion vacancies in the catalyst surface which expose the reactive metal centres. It is also accepted that the anion vacancies are in equilibrium with the pressures of hydrogen sulphide and hydrogen gas thus:



where \square denotes an anion vacancy. Increasing the hydrogen pressure at the catalyst surface under these conditions should therefore have the effect of converting adsorbed sulphur to H₂S and creating active sites for aromatic hydrogenation. From the experimental results presented above it may be concluded that, by this mechanism, sulphided nickel-tungsten on alumina responds well to large increases in the hydrogen partial pressure. Further work on nickel-tungsten catalysts undertaken by Voorhoeve and Stuiver indicated that the active sites for aromatic hydrogenation in the sulphided catalyst are W³⁺ ions and these authors postulated that hydrogenation proceeds via π -bonded adsorption complexes in which the hydrocarbons are bound to tungsten ions in the WS₂ surface (5)(6).

Some discussion explaining the difference in behaviour of the three catalysts is needed. Recently Weisser and Jaffar investigated the effect of the presence of H_2S on catalyst performance for benzene hydrogenation (7). In the absence of H_2S a sulphided nickel-tungsten on alumina catalyst was found to be much more active than cobalt-molybdenum when tested for the hydrogenation of pure benzene at $300^\circ C$ and 8 MPa hydrogen partial pressure. However, in the presence of 1 vol % H_2S a severe retardation of the hydrogenation activity was observed. The original high activity was restored upon removal of H_2S from the feed. The impeding effect of H_2S was much more pronounced in the case of the sulphided nickel-tungsten catalyst and the performance of the two catalysts became comparable in the presence of H_2S . Based on the mechanism of reaction [9], which involves the sulphiding of anion vacancies, it is apparent that these vacancies would be liable to undergo sulphiding to a different extent depending on the nature of the catalyst used. Furimsky (8) indicated that, in the bulk, MoS_2 should be a more stable sulphide than WS_2 . This difference in stability would contradict the strong poisoning effect of H_2S on the nickel-tungsten catalyst. However, it may be argued that the important sulphide stabilities are those at the surface, i.e. at the bases or edges of crystals. Also the effect of the promoting metals should not be discounted.

The Effect of Aromaticity on Diesel and Jet Fuel Combustion Quality

Figure 8 presents a plot of percent aromatic carbon versus cetane number for fuel products generated under various hydroprocessing conditions using the sulphided nickel-tungsten on alumina catalyst. In all cases the pressure was 17.3 MPa while temperature and liquid hourly space velocity were varied. The aromatic carbon content and cetane

number of the feedstock is also indicated in the plot together with the current Canadian diesel fuel specification (cetane number 40). The plot demonstrates the severity of processing required to produce good quality fuel. It is apparent from the graph that the first 50% of aromatic carbon conversion increases the cetane rating by only two points, i.e. from 36 to 38, and a 75% conversion produces a fuel of ignition quality which is still just below the specification rating. Thus, at least a 90% conversion is required in order to raise the cetane number well within the specification limit. It is apparent that the remaining aromatic hydrocarbon species are very stable and resistant to saturation under these severe hydroprocessing conditions. They also appear to have a significantly more adverse effect on diesel ignition quality than those which are removed under less severe conditions. It is significant that low concentrations of these compounds can have such a detrimental effect on fuel ignition quality.

Figure 9 presents a similar plot obtained by processing fuel products using the sulphided cobalt-molybdenum catalyst. It is noteworthy that the correlation is not as good as in Figure 8 since the plotted points show more scatter. The greater scatter is probably caused by more extensive cracking observed with the sulphided cobalt-molybdenum catalyst over the same temperature range, as mentioned previously. We may assume that saturation of aromatics is the only major process occurring when using the nickel-tungsten catalyst, the result being a smooth correlation. These graphs also reinforce the findings from the kinetic work that the cobalt-molybdenum catalyst is less suitable for saturation of aromatics in these fuels. For this catalyst, in spite of the reduced activity, the cetane number specification can still be achieved. Refer-

ence to Figure 4 shows that in order to produce good quality diesel fuel from this feedstock using the sulphided nickel-tungsten catalyst, a hydrogen partial pressure of approximately 12 MPa would be required.

A correlation of percent aromatic carbon versus smoke point determined on fuel products from hydroprocessing at different temperatures and space velocities and 17.3 MPa using the sulphided nickel-molybdenum catalyst is presented in Figure 10. The graph shows that the specification limit of 20 mm is easily surpassed using this catalyst.

The present work can be summarized as follows. Approximately 97% of the aromatic carbon in the feedstock may be converted by severe hydroprocessing over a sulphided nickel-tungsten on alumina catalyst giving a fuel product which is predominantly naphthenic. Kinetic experiments demonstrate the superiority of this catalyst over the corresponding molybdenum types for achieving the greatest conversions. The investigation established the optimum operating conditions for saturation of aromatics given that the equilibrium reaction is an important factor in determining such conditions. Cetane engine testing and correlation of ignition quality with aromatic carbon content has revealed questions about the efficiency of promoting fuel quality by means of this kind of hydroprocessing. It is apparent from these correlations that low levels of stable aromatic species may have an adverse effect on diesel fuel ignition quality. The results from hydroprocessing and engine testing also show that fuel of acceptable quality, i.e. cetane number 45, may be produced from this feedstock. Similar correlations of smoke point with aromatic carbon content reveal that this particular jet fuel specification can easily be achieved.

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- (8) Furimsky, E., Catal. Rev.-Sci. Eng., 1980, 22, 371.

CAPTIONS

- Figure 1. Plots of Relative Density of Hydrotreated Product vs Liquid Space Velocity for Sulphided Cobalt-Molybdenum and Nickel-Tungsten Catalysts.
- Figure 2. Effect of Liquid Hourly Space Velocity on Aromatics Saturation over Sulphided Nickel-Tungsten Catalyst.
- Figure 3. Effect of Liquid Hourly Space Velocity on Aromatics Saturation over Sulphided Cobalt-Molybdenum Catalyst.
- Figure 4. Effect of Hydrogen Pressure on Aromatics Saturation over Sulphided Nickel-Tungsten Catalyst.
- Figure 5. Pseudo-First-Order Reversible Kinetics for Aromatics Saturation over Sulphided Cobalt-Molybdenum and Nickel-Molybdenum Catalysts.
- Figure 6. Pseudo-First-Order Reversible Kinetics for Aromatics Saturation over Sulphided Nickel-Tungsten Catalyst.
- Figure 7. Arrhenius Plot of Pseudo-Rate Constants for Aromatics Saturation.

Figure 8. Correlation of Product Cetane Number with Aromatic Carbon Content by C^{13} NMR. Reactions over Sulphided Nickel-Tungsten Catalyst.

Figure 9. Correlation of Product Cetane Number with Aromatic Carbon Content by C^{13} NMR. Reactions over Sulphided Cobalt-Molybdenum Catalyst.

Figure 10. Correlation of Smoke Point (ASTM D1322) with Aromatic Carbon Content of Product by C^{13} NMR. Reactions over Sulphided Nickel-Molybdenum Catalyst.

TABLE 1. Properties of Middle-Distillate Feedstock

| | |
|--|-------|
| Relative Density, 15/15°C | 0.836 |
| Carbon (wt %) | 87.46 |
| Hydrogen (wt %) | 12.47 |
| Sulphur (wt %) | 0.055 |
| Nitrogen (ppm) | 54 |
| Average Molecular Weight | 201 |
| % Aromatic Carbon by C ¹³ NMR | 14.3 |
| Cetane Number | 36 |
| Distillation (D 86) | |
| IBP °C | 142 |
| 10% | 181 |
| 50% | 232 |
| 90% | 283 |
| FBP | 333 |

TABLE 2. Catalyst Properties

| <u>Catalyst</u> | |
|--|--|
| CoO-MoO ₃ /γ-Al ₂ O ₃ | <p data-bbox="659 710 1105 741"><u>Cyanamid Aero Trilobe HDS-20</u></p> <p data-bbox="659 772 1317 897">Containing: 10.8 wt % Mo and 3.9 wt % Co Surface area: 230 m²/g Pore volume: 0.43 cc/g Extrudates of 2.5 mm average diameter</p> |
| NiO-MoO ₃ /γ-Al ₂ O ₃ | <p data-bbox="659 932 980 963"><u>Cyanamid Aero HDS-9A</u></p> <p data-bbox="659 994 1284 1118">Containing 11.7 wt % Mo and 2.5 wt % Ni Surface area: 170 m²/g Pore volume: 0.39 cc/g Extrudates of 1.5 mm average diameter</p> |
| NiO-WO ₃ /γ-Al ₂ O ₃ | <p data-bbox="659 1152 1045 1183"><u>Katalco Sphericat NT-550</u></p> <p data-bbox="659 1214 1300 1338">Containing: 15.8 wt % W and 3.9 wt % Ni Surface area: 200 m²/g Pore volume: 0.58 cc/g Spheres of 3.2 mm average diameter</p> |

TABLE 3. Activation Energies and Log Pre-exponential Factors for Saturation of Aromatics

| Catalyst (sulphided) | Feed | Activation Energy KJ/mole | ln A |
|--------------------------------------|------------|---------------------------------|------------|
| Co-Mo/Al ₂ O ₃ | this study | 63 ± 9 | 10.5 ± 1.8 |
| Ni-Mo/Al ₂ O ₃ | this study | 83 ± 3 | 14.7 ± 0.5 |
| Ni-W/Al ₂ O ₃ | this study | 60 ± 4 | 10.6 ± 0.8 |
| Ni-W/Al ₂ O ₃ | Benzene | 71 | - |

FIG. 1

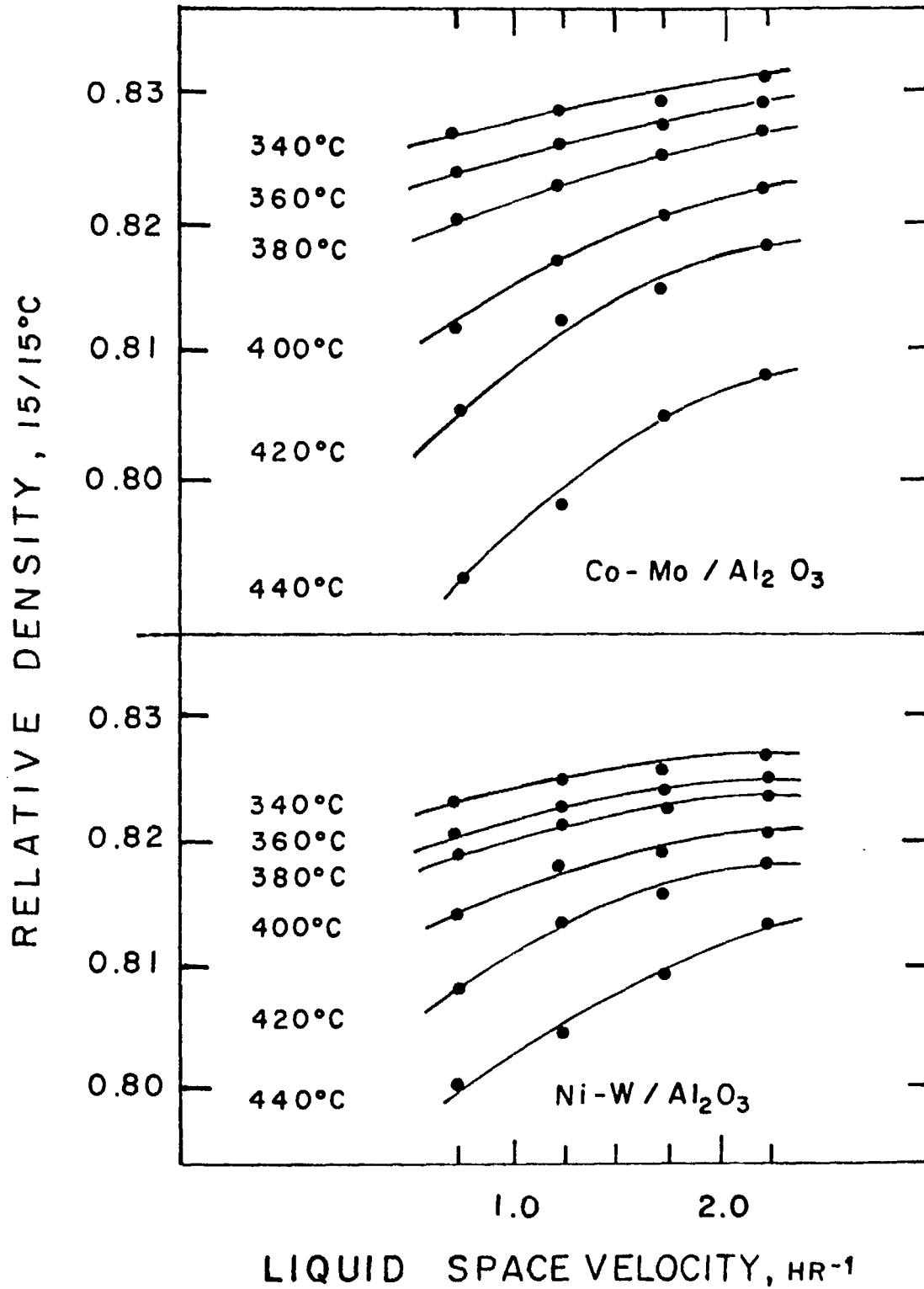


FIG. 2

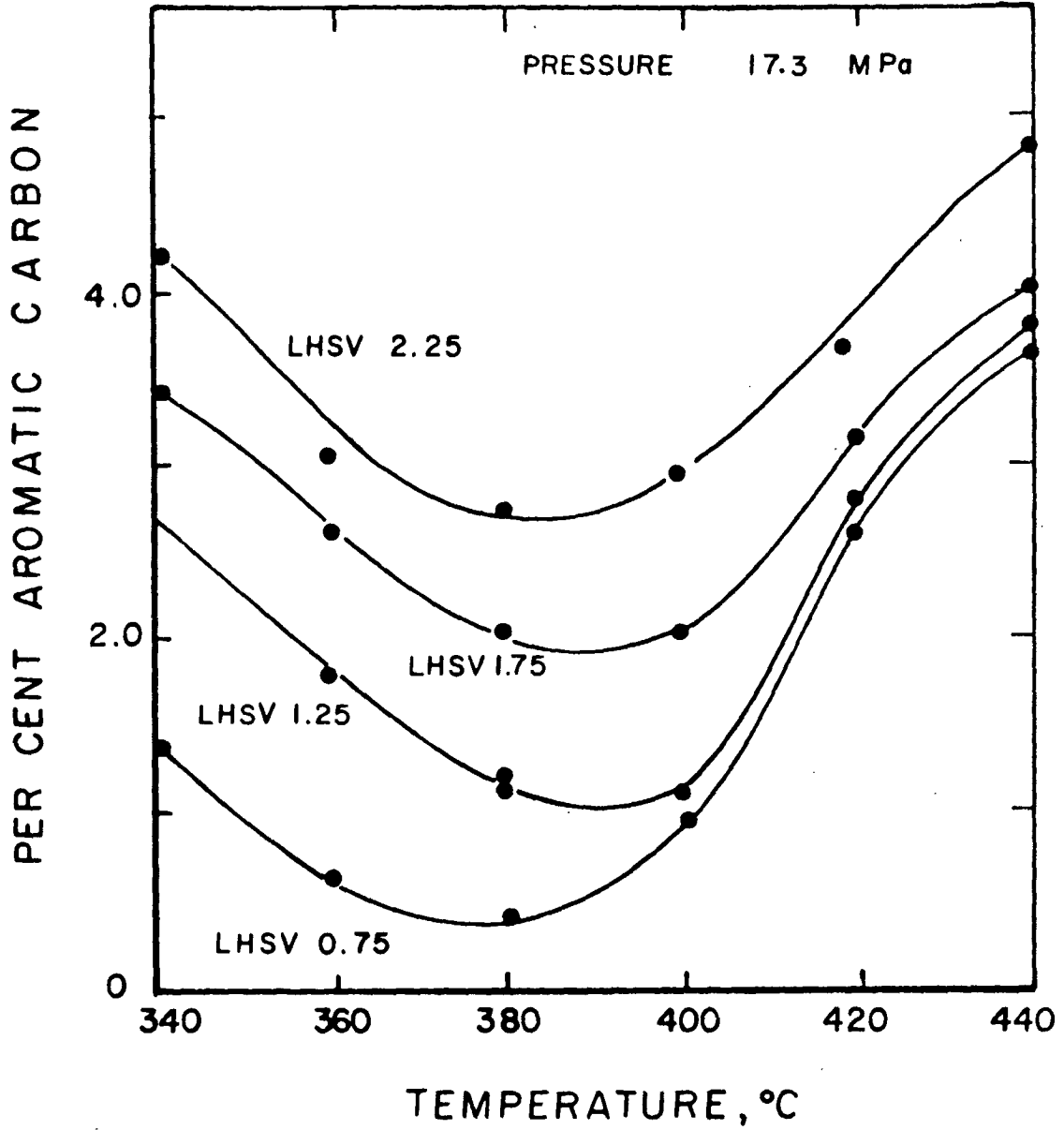


FIG. 3

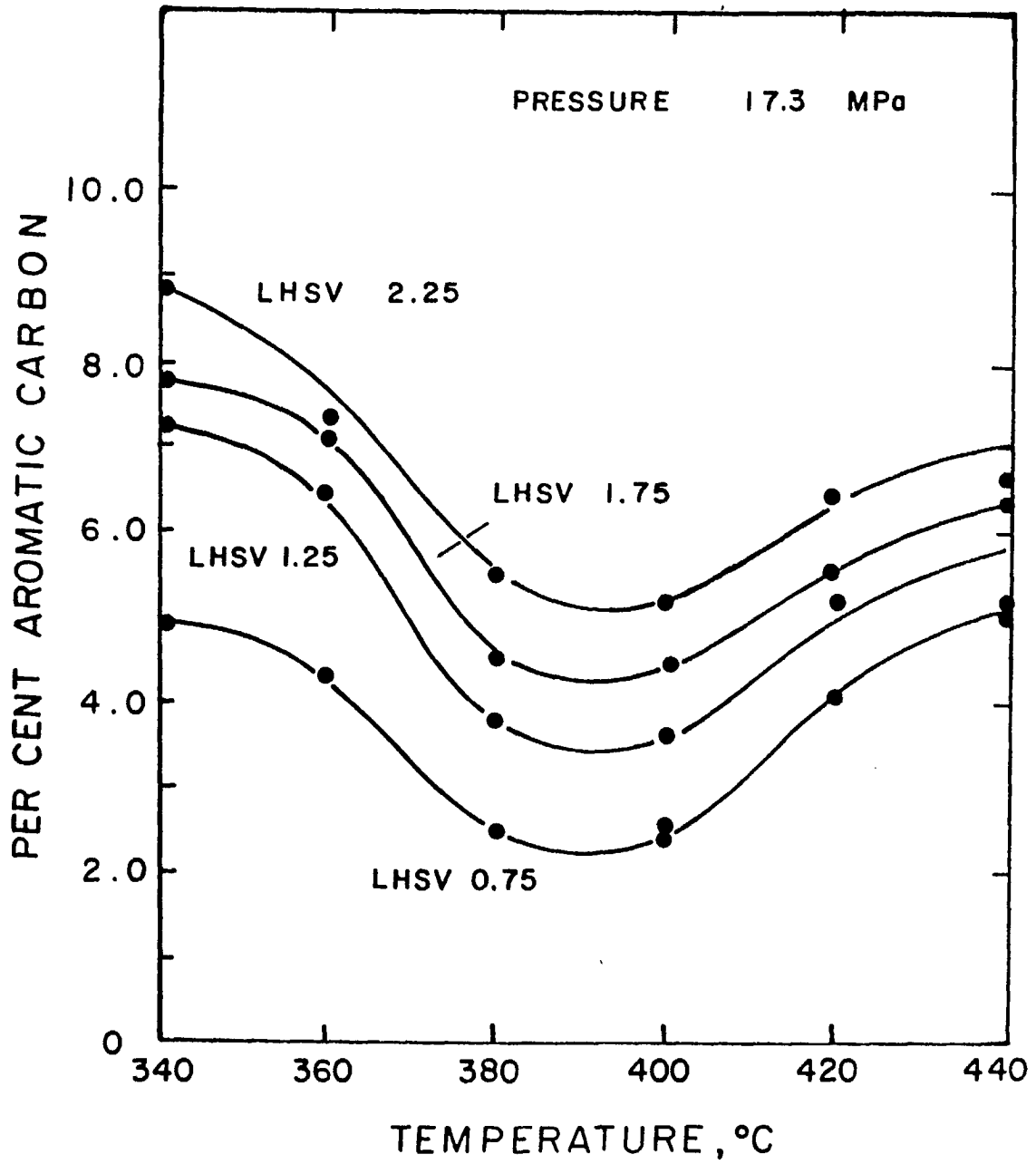
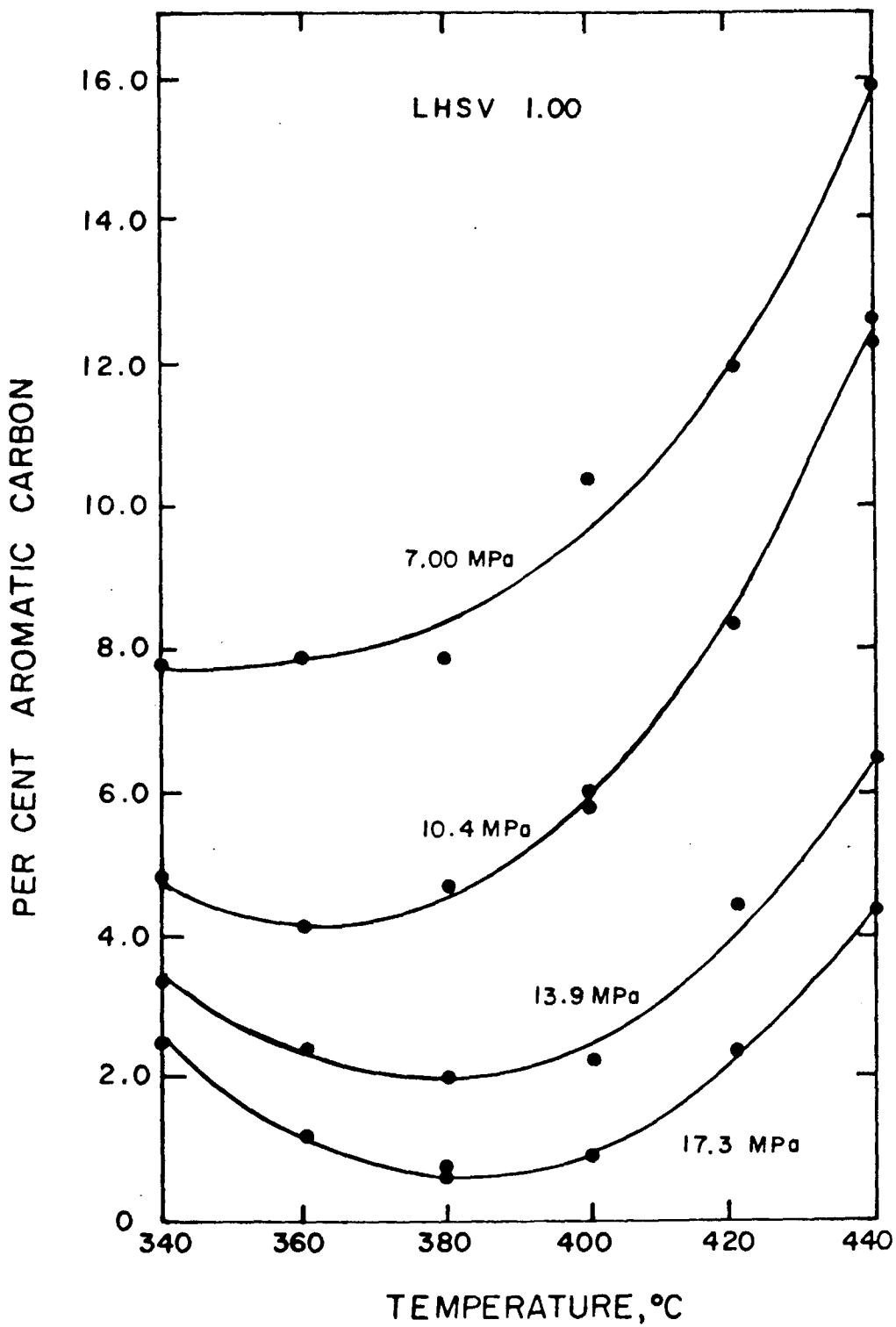
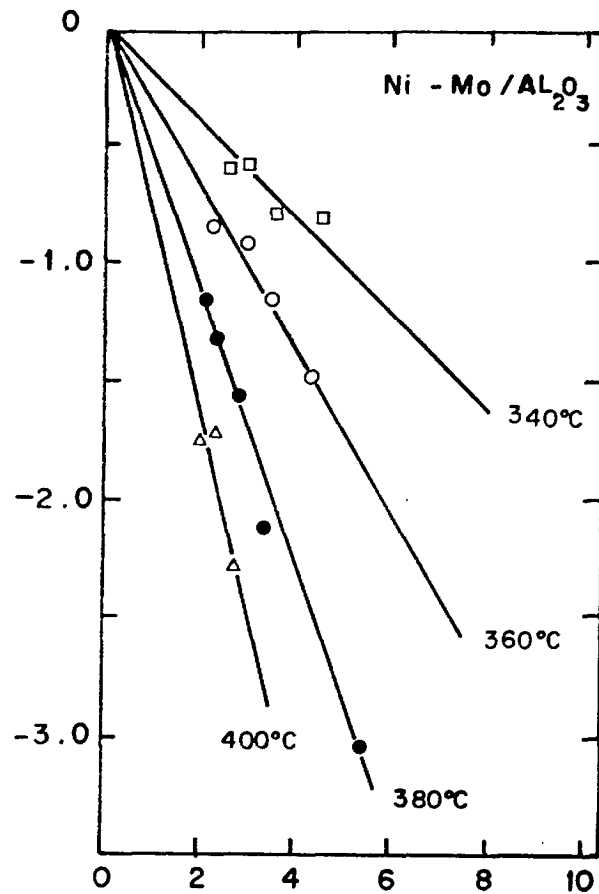
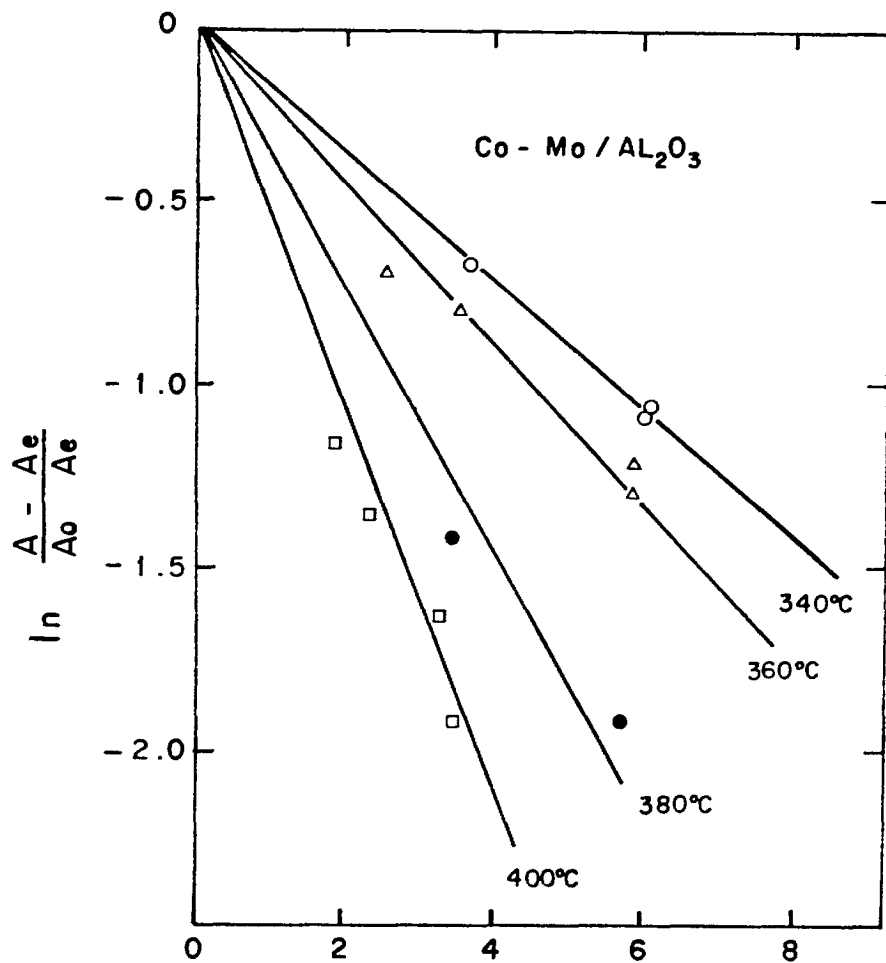


FIG. 4





TIME, min

FIG. 5

FIG. 6

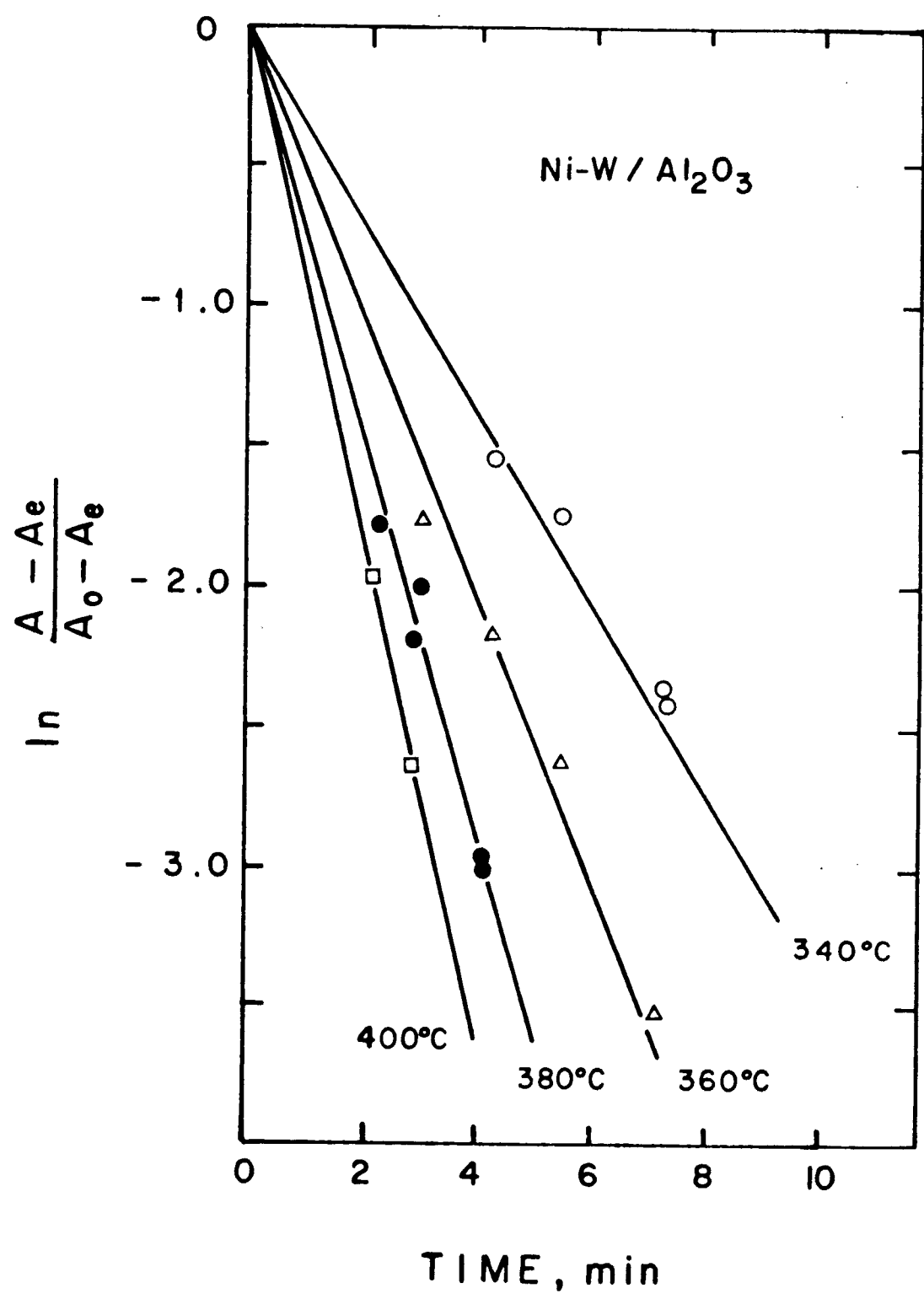
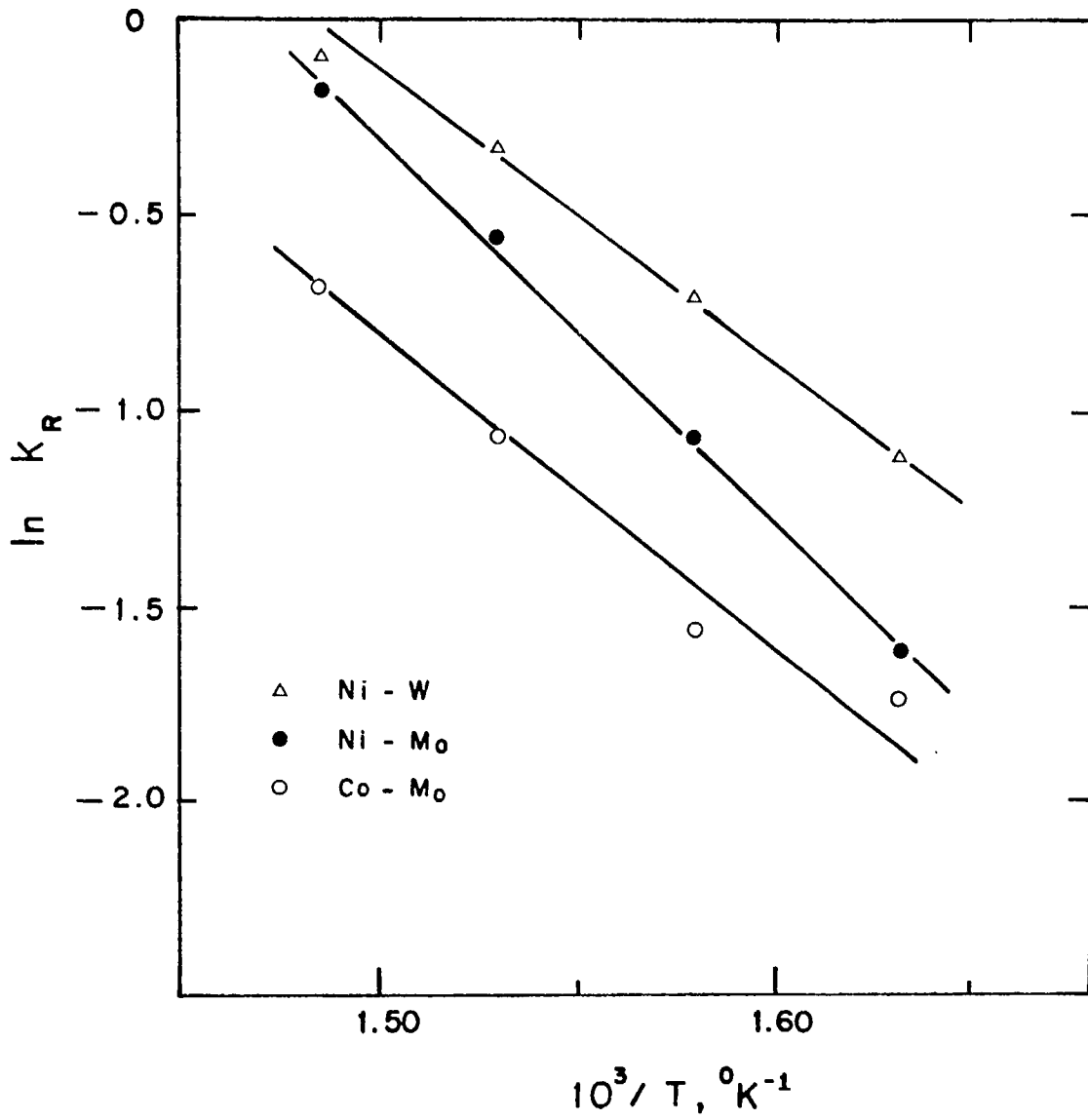


FIG. 7



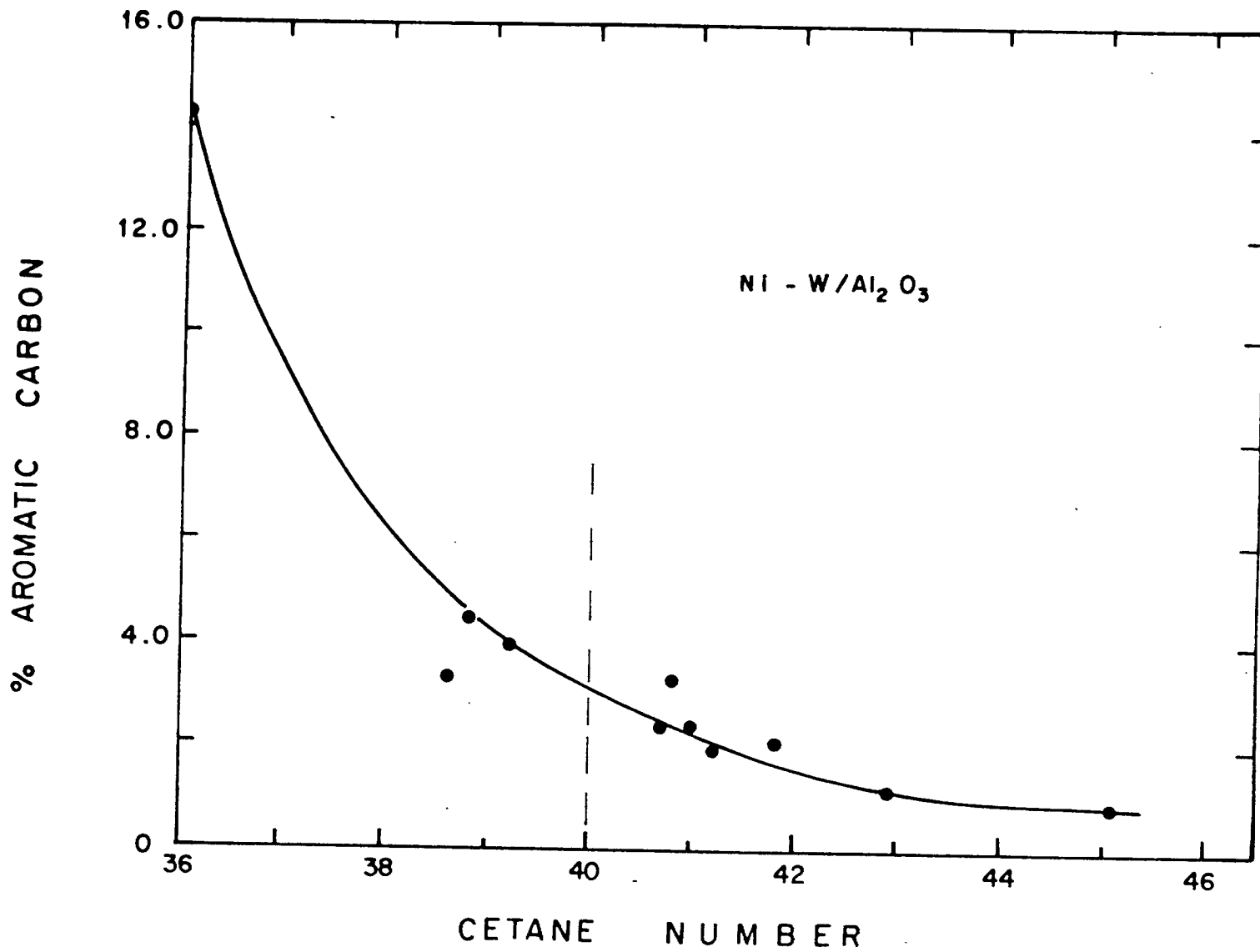


FIG. 8

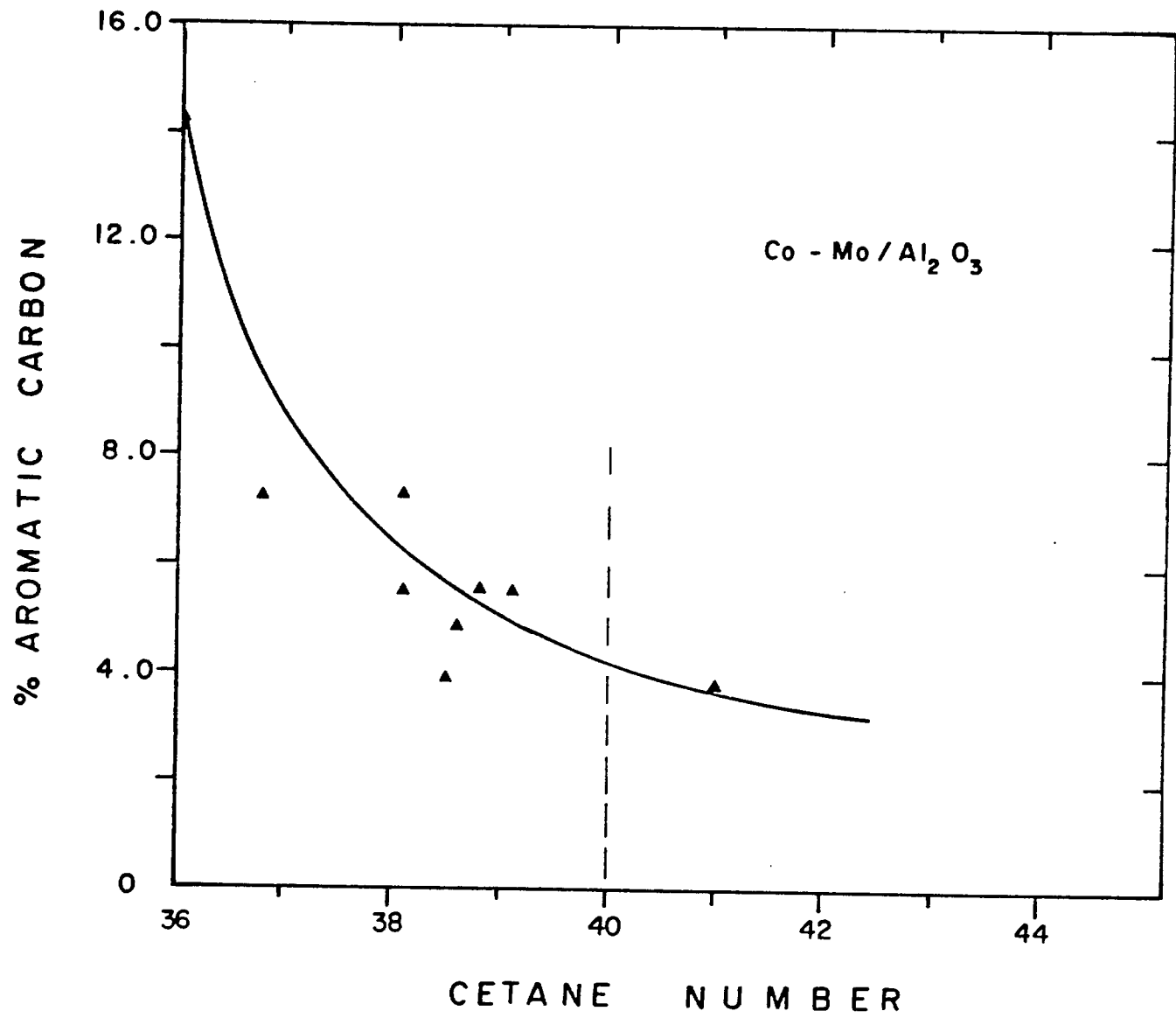


FIG. 9

FIG. 10

