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SELECTED ASPECTS OF CATALYTIC REFINING OF MIDDLE DISTILLATES FROM ATHABASCA SYNCRUDES

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ABSTRACT

Production of specification diesel fuels from Athabasca oil sands may be achieved by additional input of hydrogen to saturate excessive aromatic concentrations in middle distillates. Hydroprocessing of syncrude distillates from fluid coked Athabasca bitumen was carried out over a sulfided nickel-tungsten catalyst using semi-pilot plant hydrotreaters.

Severe hydrotreating pressures were used to generate a series of fuel products over a wide temperature range. Compositional analyses of feedstock and products were performed using low resolution mass spectrometry. Aromatic carbon content was determined by C^{13} NMR. By this means the effect of hydroprocessing temperature and LHSV on aromatics conversion was monitored. Differences in reactivity including the effects of thermodynamic equilibria and cracking were observed for various aromatic species. Engine tests performed provided the relationship between the aromatic content and the cetane rating of the products obtained. Some data previously published for distillates from delayed coking are included for comparison.

RESUME

On peut effectuer la production de combustibles spécifiés pour moteur diesel à partir des sables bitumineux de l'Athabasca en ajoutant de l'hydrogène comme agent de saturation des concentrations aromatiques excessives dans des distillats moyens. On a hydrotraité des distillats des pétroles synthétiques provenant du bitumen liquide cokéfié de l'Athabasca en utilisant un catalyseur sulfuré de nickel-tungstène avec des hydrotraitants des installations semi-pilotes. On a employé des pressions d'hydrotraitement rigoureuses dans le but de créer une série de produits combustibles dans une grande gamme de températures. On a analysé la composition des matières premières et des produits au moyen de la spectrométrie de masse à faible résolution. La teneur en carbone aroma-

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tique a été déterminée par la méthode de C^{13} NMR. De cette façon on a pu contrôler l'effet de la température d'hydrotraitement et la LHSV sur la conversion des aromatiques. On a observé les différences de réactivité, y compris les effets de l'équilibre thermodynamique et du craquage, des diverses espèces d'aromatiques. Des essais de moteur ont fourni le rapport entre la teneur en aromatiques et l'indice de cétane des produits obtenus. On a inclus, comme documentation de comparaison, des données publiées précédemment sur les distillats de la cokéfaction retardée.

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MIDDLE DISTILLATES FROM ATHABASCA SYNCRUCDES

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INTRODUCTION

The two existing commercial processes for upgrading Athabasca bitumen use delayed and fluid bed coking and produce synthetic crudes which are low in paraffins and relatively high in aromatics and naphthenes. The problems of producing specification transportation fuels from these feedstocks have been discussed in earlier reports (1,2). In previous work, middle distillates from delayed coking of bitumen were catalytically refined by severe hydroprocessing using conventional hydrotreating catalysts. The aromatics conversion to naphthenes was monitored using C^{13} NMR analysis and the kinetics of hydrogenation was elucidated together with the effects of thermodynamic equilibria (2).

The present work deals with hydroprocessing of middle distillates from fluid coked bitumen and uses low resolution mass spectrometry to provide compositional analyses of the fuel products generated. The mass spectrometric method allows the determination of differences in reactivity of aromatic and saturated

compound types including the effects of thermodynamic equilibria and cracking. Cetane numbers of fuel products were determined by engine tests and the relationships obtained between aromatic content and cetane rating are compared with previous results obtained for refined distillates from a delayed coking process.

EXPERIMENTAL

The feedstock used in this study was a middle distillate fraction from a synthetic crude produced by fluid coking of Athabasca bitumen. Table I presents properties of the feedstock. A commercial $\text{NiO-WO}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst (Katalco Sphercat NI-550), tested in a previous study, was used for hydroprocessing the feed (2,3).

A detailed description of the semi-pilot plant hydrotreating system is given in an earlier report (2). The experimental runs were carried out using 70 grams of catalyst in 100 cc of reactor volume. The catalyst was sulfided at 380°C and atmospheric pressure by passing a mixture of 10% H_2S in hydrogen over the bed for 2 hours. The volume of H_2S passed was equivalent to eight times the amount of sulfur required for the formation of sulfides. The continuous flow reactor was operated in the up-flow mode, the liquid feed and hydrogen were mixed, passed through a pre-heater and then over the fixed bed of catalyst. The unit was run for 8 hours on oil before the first steady-state sample was taken. Experimental runs were performed at temperatures of $340\text{--}440^\circ\text{C}$, liquid space velocities of 0.75 to 2.00 hr^{-1} and a hydrogen flow rate at SIP of 530 L hydrogen per L of feedstock (3000 scf/bbl). All runs were at a pressure of 17.3 MPa (2500 psig). The reactor system was maintained at steady-state conditions for 1 hr prior to and 2 hrs during the period in which product was collected.

Compositional analysis of the feedstock and hydrotreated products was performed by low resolution mass spectrometry using a modification of the method of Robinson (4). The samples were run on a CEC 103 mass spectrometer. The aromatic carbon content was determined by C^{13} NMR analysis using a Varian SL-200 spectrometer. Sulfur content was analyzed by the Wickbold technique and carbon, hydrogen and nitrogen analysis was carried out using a Perkin Elmer 240B analyzer.

Cetane numbers were determined on a standard Cooperative Fuels Research (CFR) test engine using a constant compression ratio method.

RESULTS AND DISCUSSION

Hydrocarbon Compositions and Effects of Processing

The chemical characteristics of middle distillates from the Athabasca syncrudes are significantly different from those of conventional crudes. This is a consequence of the unique oil sands compositions and the upgrading processes employed. The mass spectrometric method used in this work allows the identification of a number of distinct hydrocarbon group types and the amount of each group type found in a particular fuel is a function of the feedstock source and processing conditions.

Table II shows compositional analyses of middle distillates from two Athabasca syncrudes produced by fluid and delayed coking of bitumen and designated A and B respectively. Also included are compositions of products from secondary hydrotreating of the above distillates from this and previous work. The distillates are from approximately the same boiling range (2,3).

A comparison of distillates from syncrudes A and B shows some important differences in their chemical compositions. Syncrude A (from fluid coking) yields distillate which is significantly lower in paraffins (15.8%) than that from B (26.4%). (Distillate from A is also marginally lower in total cycloparaffins). The aromatic contents of the two distillates are also significantly

different with distillate from A having an amount which is approximately 17% higher. To some extent this may be attributed to differences in severity of primary hydrotreating. These major differences in chemical composition are reflected in the cetane numbers 31 and 36 for A and B respectively.

A comparison in Table II of products from the syncrudes after secondary hydrotreating (this work together with earlier results) shows almost complete elimination of aromatics under the given processing conditions and these results confirm previous analysis by C^{13} NMR. Both products show a marginal increase in paraffins which indicates some cracking, possibly ring scission of cycloparaffins.

An examination of the aromatic hydrocarbon group types in Table II shows major contributions from 4 predominant species in syncrude distillates (alkylbenzenes, benzocycloparaffins, benzodicycloparaffins and naphthalenes). The saturation of these species is therefore the major contributing factor in cetane improvement. Figure I shows summarized chemical changes for conversion of some of the aromatic group types to their corresponding naphthenes. This work also demonstrates that such reactions are controlled by thermodynamic equilibria.

In previous work, where C^{13} NMR was used to monitor the effects of changing experimental conditions on aromatics conversion, plots of aromatic carbon content vs. temperature were made, the processing effects were "mapped out" with changing LHSV and optimum operating conditions were established (2,3). In the present work some of the implicit relationships between the kinetic and thermodynamic equilibrium effects (including cracking) are resolved by separately mapping out the individual hydrocarbon group types.

Figure 2 shows the effect of change of LHSV on the mass % of alkylbenzenes in product from secondary hydrotreating of syncrude A distillate over the complete temperature range. A series of smooth, round, almost symmetrical curves is obtained showing a minimum at 380-400°C. Above this temperature the effect of

thermodynamic equilibrium is observed as the concentration of alkylbenzenes increases again. It is assumed that cracking occurring under these processing conditions for this equilibrium reaction is not significant.

On the other hand, Figure 3, which is a similar plot for saturation of benzocycloparaffins, produces a series of v-shaped curves which show a marked loss of roundness above 380°C. Figure 3 may be linked with Figure 4 which shows corresponding plots for conversion of benzodicycloparaffins (see Figure 1). In this case it is clear that extensive cracking during this particular equilibrium reaction occurs above 400°C and the curves pass through a maximum at 420°C. It is assumed that, in this high temperature range, ring scission in a 3-ring structure occurs with the generation of a corresponding 2-ring species.

Mass spectrometric analysis also suggests that some cleavage of two-ring structures occurs under extreme processing conditions. Figure 5 shows plots of condensed dicycloparaffin mass % vs LHSV over the complete temperature range. As expected, the curves produced are more or less the mirror image of Figure 3 (the corresponding plots for benzocycloparaffins) and pass through a maximum at 370-380°C as a result of the equilibrium shift. The curves indicate that although the dicycloparaffins seem reasonably stable for most of the observed conditions, some cracking is likely at low space velocities (0.75 and 1.00) and at higher temperatures (crossing of curves in Figure 5). Figure 6 is a similar plot for the condensed polycycloparaffins in which case extensive cracking is observed at temperatures as low as 360-380°C. These reactions may be important for fuel quality improvement by ring opening of naphthenes.

Effect of Aromatic Content on Fuel Ignition Quality

Figure 7 shows a plot of % aromatic carbon content (determined by C^{13} NMR) versus cetane number for fuel products produced by secondary hydrotreating of distillates from syncrudes A and B under different conditions of temperature and LHSV. These plots reveal the processing severities required to produce fuels which meet the current Canadian diesel ignition specification (cetane number 40).

The curvature of these graphs has been attributed to the presence of very stable aromatic species which would appear to have a markedly adverse effect on diesel ignition quality (3).

The plots indicate qualitative differences between syncrudes A and B. For any level of aromatic content, the syncrude produced by delayed coking shows better cetane rating. Most likely, it is a consequence of the higher paraffin content in this feedstock.

SUMMARY

Secondary hydrotreating was performed on a middle distillate from a syncrude produced by fluid coking of Athabasca bitumen and products were analyzed by low resolution mass spectrometry. The processing effects on several hydrocarbon group types were "mapped out" in terms of temperature and LHSV. It was concluded that alkylbenzene and benzocycloparaffin saturation is accompanied by a minimum of cracking but for the equilibrium reaction involving saturation of benzodicycloparaffins, cracking was observed above $400^{\circ}C$ at all space velocities. The cracking of polycycloparaffins was also found to be extensive by examining the corresponding plots for these hydrocarbon group types.

The effects of aromatic content on fuel ignition quality of the two syncrudes were compared. Although the trends were remarkably similar, consistent differences in quality were observed throughout the range.

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TABLE I

PROPERTIES OF MIDDLE-DISTILLATE FEEDSTOCK
FROM SYNTHETIC CRUDE A
(FLUID COKED BITUMEN)

Relative Density, 15/15°C	0.862
Carbon	87.2 wt%
Hydrogen	11.7 wt%
Sulfur	97 ppm
Nitrogen	37 ppm
Average molecular weight	200
% Aromatic carbon by C ¹³ NMR	16.9
Cetane Number (CCR method)	31
Distillation (D86)	
IBP°C	163
5%	183
10%	192
20%	210
50%	251
90%	296
FBP	318

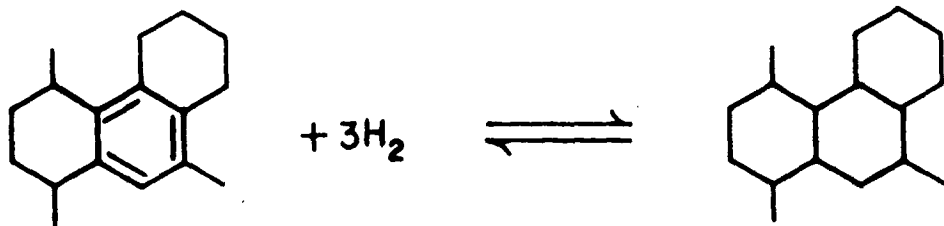
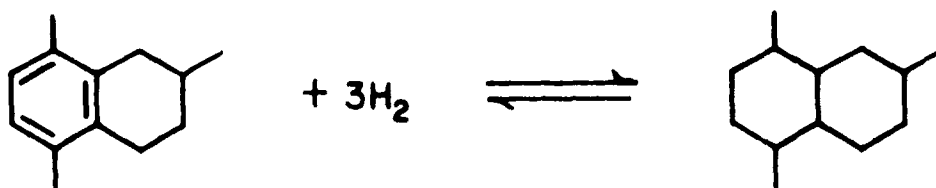
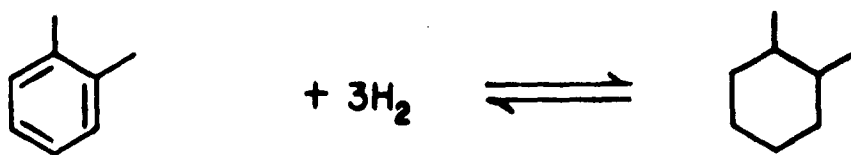
TABLE II

COMPOSITIONAL ANALYSES (MASS %) OF MIDDLE DISTILLATES FROM
ATHABASCA SYNCRUDES BEFORE AND AFTER SECONDARY HYDROTREATING

(Experimental Conditions: 380°C, 17.3 MPa, LHSV 0.75)

	<u>Synthetic Crude A</u>	<u>Product from A</u>	<u>Synthetic Crude B</u>	<u>Product from B</u>
	Fluid Coked Bitumen with Primary Hydrotreating	Secondary Hydrotreating of Distillate from A (this work)	Delayed Coked Bitumen with Primary Hydro- treating	Secondary Hydrotreating of Distillate from B (Ref 2,3)
Paraffins	15.8	19.5	26.4	27.2
Total Cyclo paraffins	42.4	79.3	48.9	69.6
Non-Condensed Monocycloparaffins	20.5	39.2	24.5	32.2
Condensed Dicycloparaffins	14.4	28.3	16.8	26.3
Condensed Polycycloparaffins	7.5	11.8	7.6	11.1
Total Aromatics	41.9	1.3	24.8	3.1
Alkylbenzenes	17.3	-	11.3	0.9
Benzocycloparaffins	12.9	0.5	8.7	1.3
Benzodicycloparaffins	5.2	0.6	2.6	0.6
Naphthalenes	3.5	0.2	1.6	0.3
Naphocycloparaffins	1.6	-	0.1	-
Fluorenes	1.0	-	0.5	-
Iriaromatics	0.4	-	-	-
Cetane Number	31	42.5	36	45

1. MONOAROMATIC REDUCTION TO SATURATES



2. DIAROMATIC REDUCTION

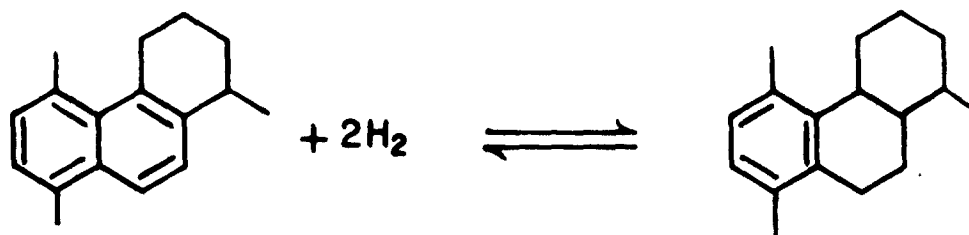
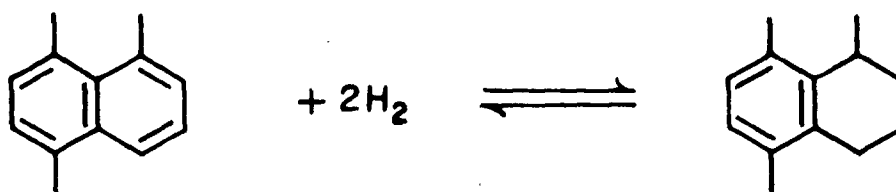


FIGURE 1. SUMMARIZED CHEMICAL CHANGES DURING HYDROTREATING OF MIDDLE DISTILLATES FROM SYNTHETIC CRUDE.

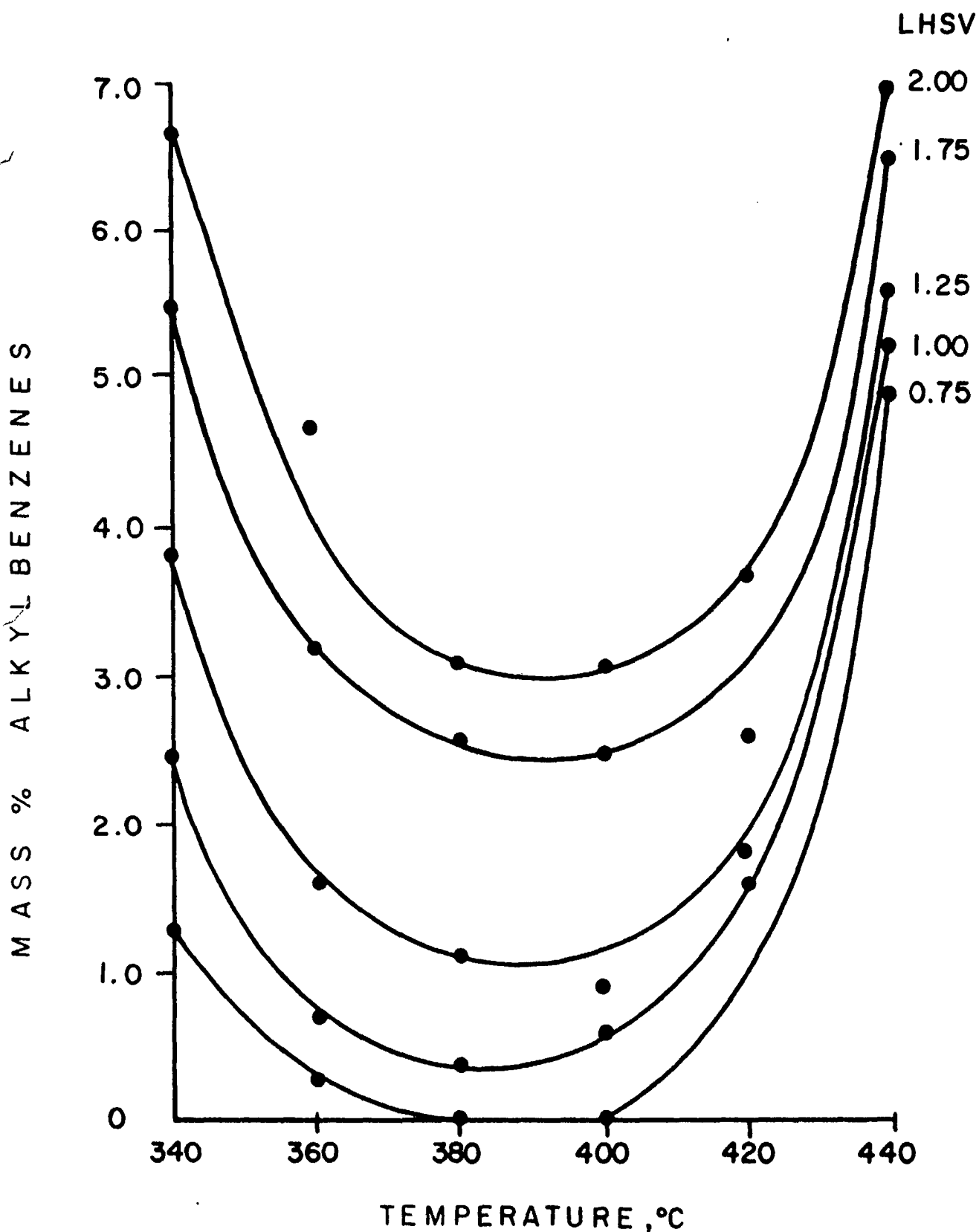


FIGURE 2. EFFECT OF LHSV ON SATURATION OF ALKYL BENZENES IN DISTILLATE FROM SYNCRUDE A (17.3 MPa).

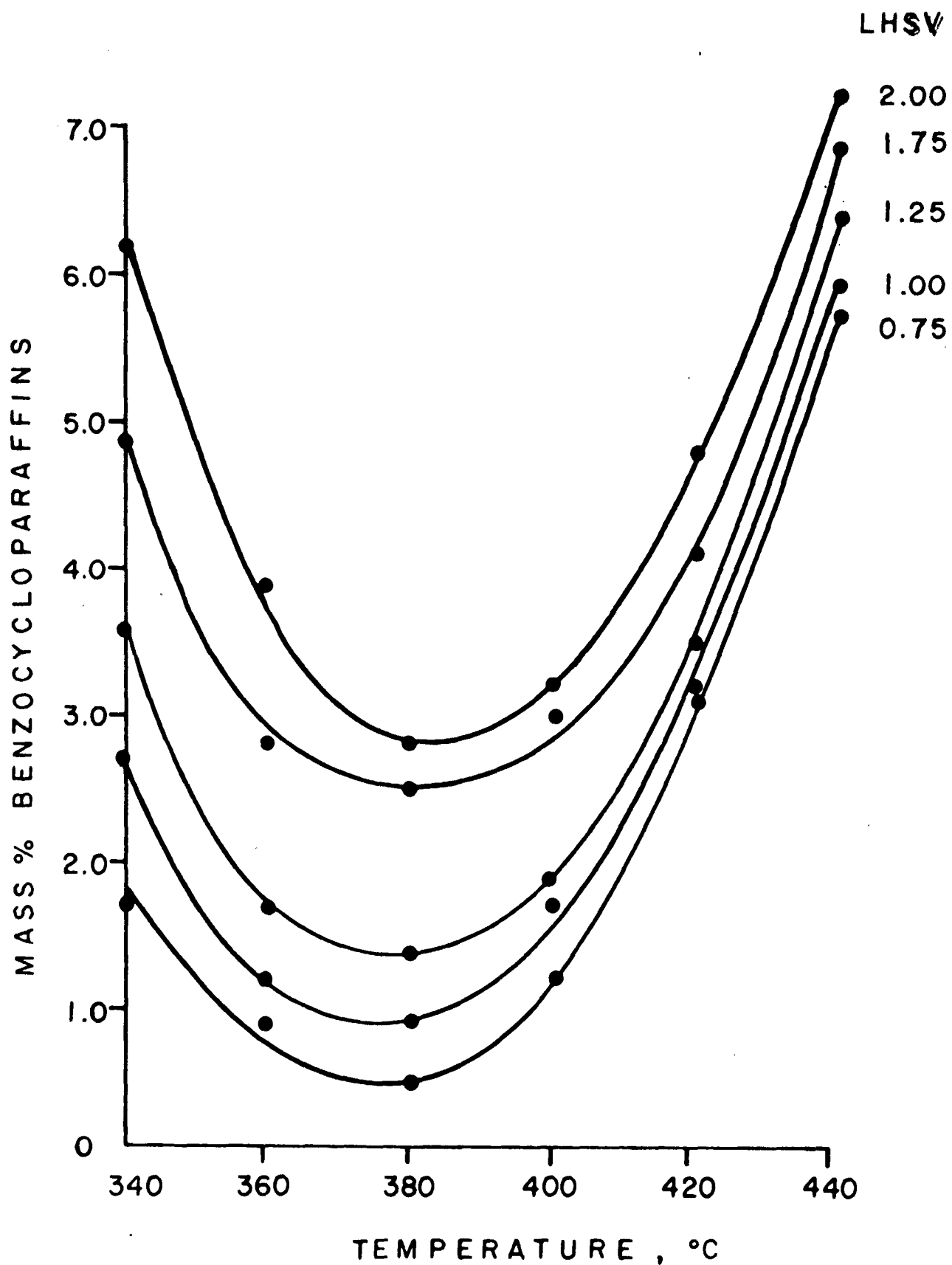


FIGURE 3. EFFECT OF LHSV ON SATURATION OF BENZOCYCLOPARAFFINS IN DISTILLATE FROM SYNCRUDE A (17.3 MPA).

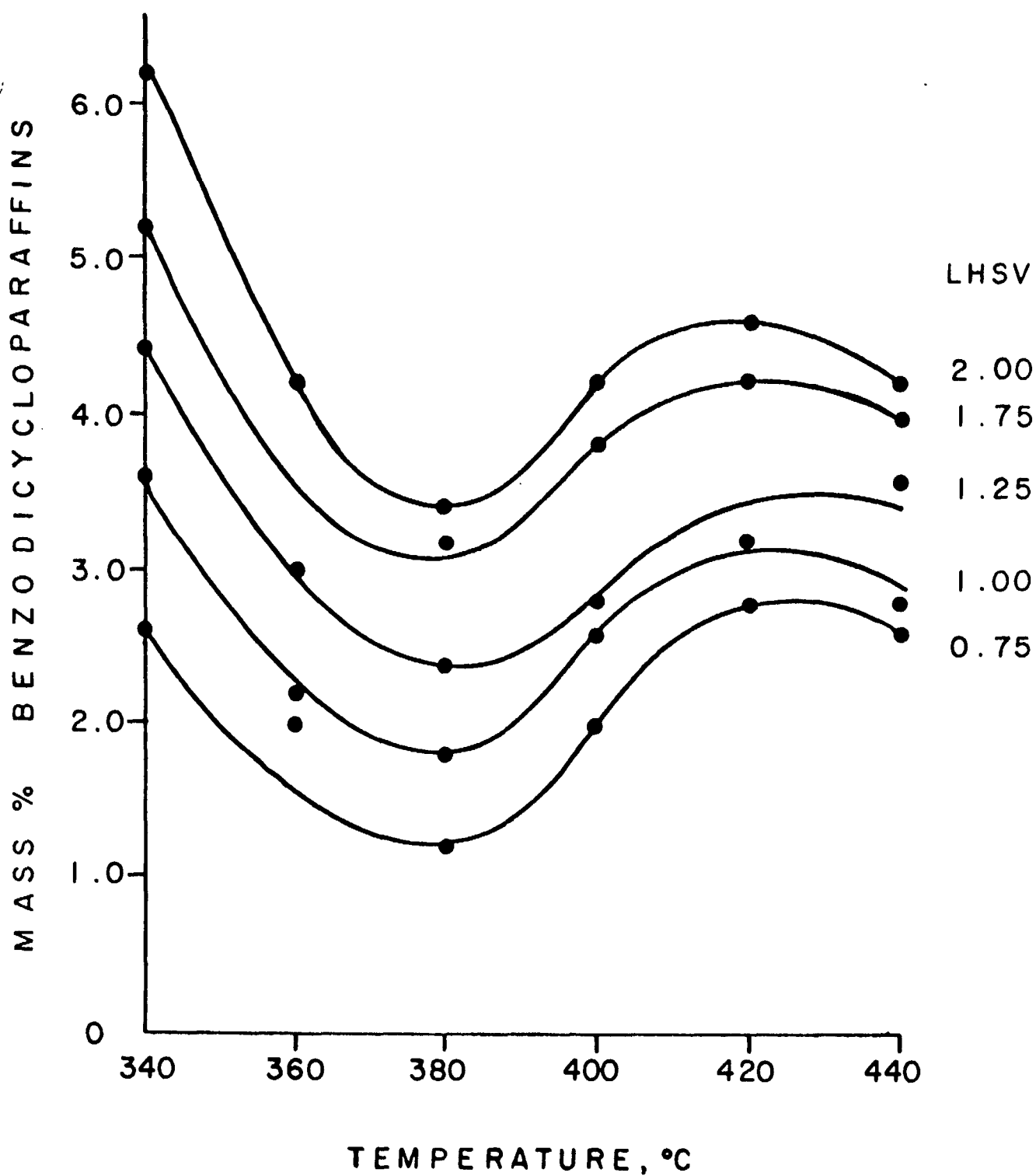


FIGURE 4. EFFECT OF LHSV ON SATURATION OF BENZODICYCLOPARAFFINS IN DISTILLATE FROM SYNCRUDE A (17.3 MPa).

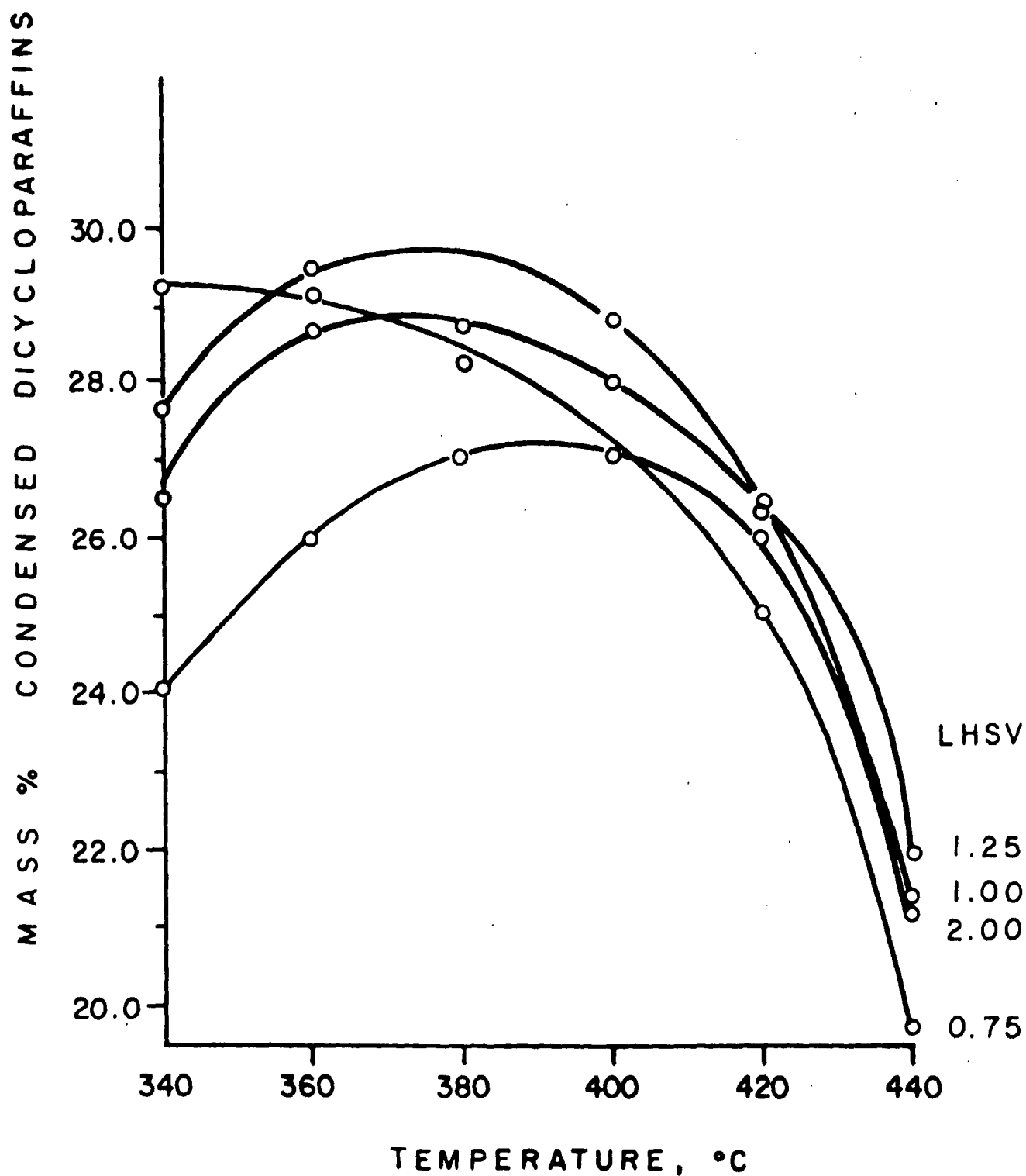


FIGURE 5. FORMATION AND DEHYDROGENATION OF CONDENSED DICYCLOPARAFFINS. EFFECT OF LHSV. (SYNCRUDE A DISTILLATE).

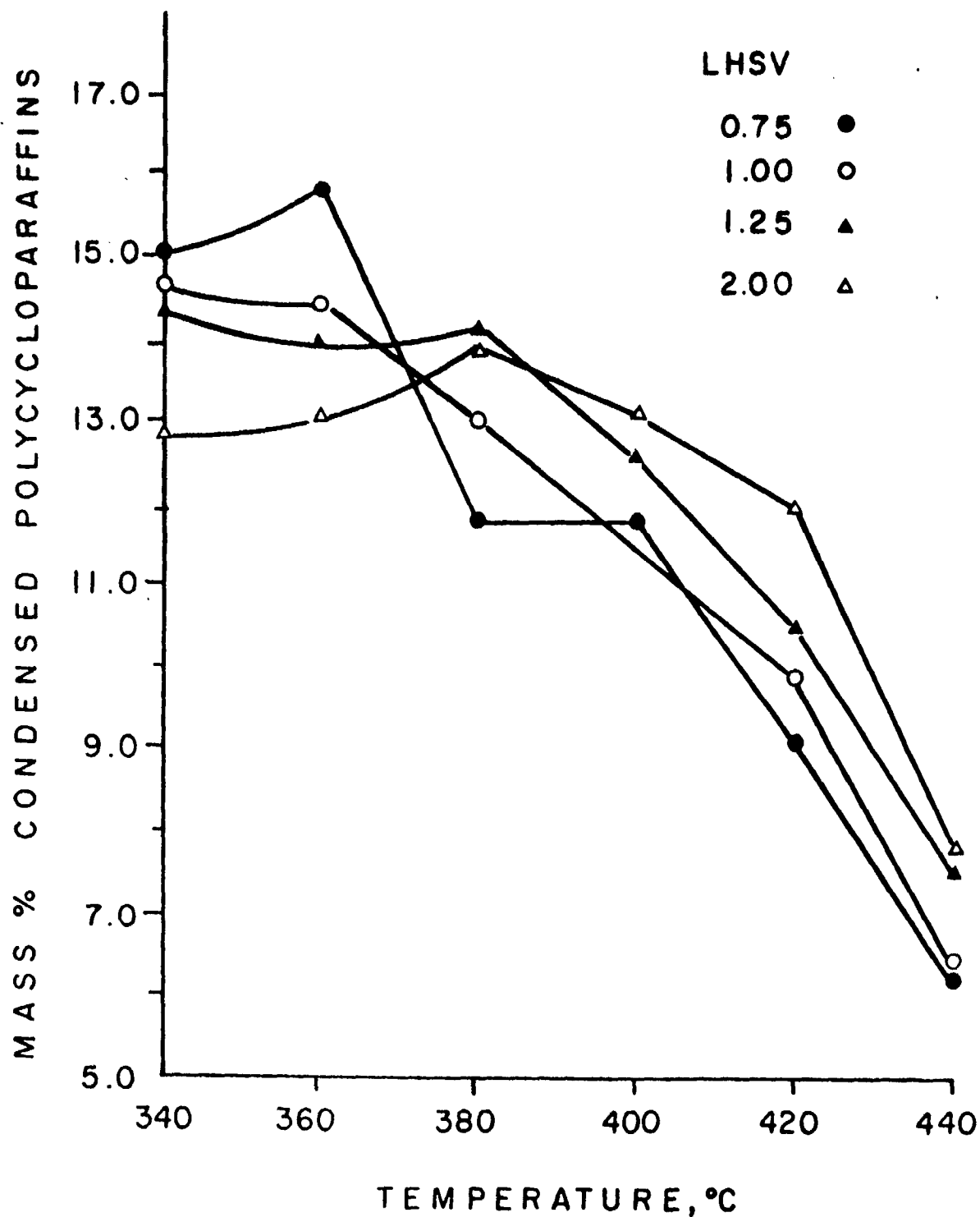


FIGURE 6. DEHYDROGENATION AND CRACKING OF CONDENSED POLYCYCLOPARAFFINS. EFFECT OF LHSV. (SYNCRUDE A DISTILLATE).

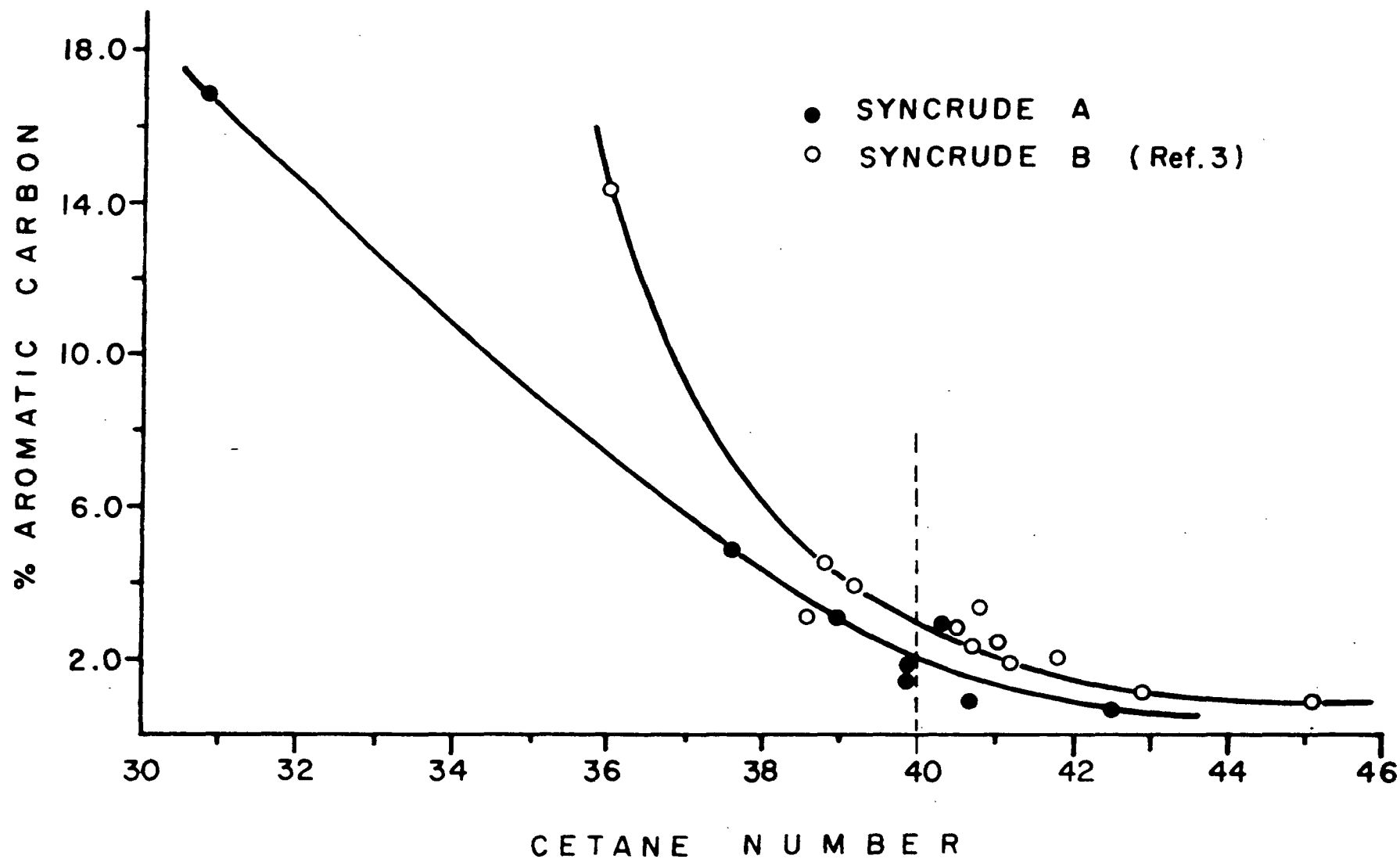


FIGURE 7. PERCENT AROMATIC CARBON (C^{13} NMR) VS. CETANE NUMBER FOR HYDROTREATED DISTILLATES FROM SYNCRUDES A AND B.