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CETANE IMPROVEMENT OF MIDDLE DISTILLATES FROM OIL
SANDS BY CATALYTIC HYDROPROCESSING

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NOVEMBER 1984

Symposium on the Chemistry of Cetane Number Improvement
Presented before the Division of Petroleum Chemistry Inc.
American Chemical Society, Miami Beach Meeting
April 28 - May 3, 1985

ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
REPORT ERP/ERL 84-55 (OP)(J)

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INTRODUCTION

In recent years, increased activity in the production of synthetic crudes from a variety of natural resources has led to the development of unique transportation fuels. Because of their unusual chemical compositions and often correspondingly poor qualities, such fuels place greater demands on conventional engine combustion processes. To some extent these problems have stimulated a greater drive towards developing new engine designs to accommodate poorer quality fuels, but a great deal of the effort needed will be in distillate refining and this will mean the development of new processes.

With future developments concerning the production of synthetic crudes from heavy oils, oil sands and coal, it is expected that primary upgrading processes will continue to yield middle distillates which are low in paraffins and relatively high in aromatics and naphthenes. The simplest approach for correcting the imbalance of saturates and improving the ignition and combustion qualities of these potential transportation fuels (jet and diesel) is to input hydrogen by conversion of aromatics to naphthenes.

An examination is made of some of the relationships found between fuel aromaticity and ignition properties. The efficiency of hydroprocessing on fuel quality improvement is also evaluated in terms of hydrogen consumption.

EXPERIMENTAL

The feedstock was a middle distillate fraction cut from a synthetic crude oil produced by fluid-bed coking of Athabasca bitumen (synthetic crude A). Properties of the feedstock are presented in Table 1. Samples of fuel products were generated by secondary hydrotreating the feed over a sulfided commercial $\text{NiO-WO}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst (Katalco Sphericat NT-550) evaluated in a previous study (1).

A detailed description of the bench-scale hydrotreating system was presented earlier (2). Hydroprocessing runs were carried out using 70 g of catalyst in 100 cm³ of

reactor volume. The catalyst sulfiding procedure was given earlier (1). The continuous flow reactor was operated in the up-flow mode, the liquid feed and hydrogen were mixed, passed through a pre-heater, then over a fixed catalyst bed. Experimental runs were carried out from 340 to 440°C, liquid space velocities of 0.75-2.00 h⁻¹ and hydrogen pressures of 7.00-17.3 MPa (500-2500 psig). A hydrogen flowrate at STP of 530 m³ (hydrogen) m⁻³ (feed-stock)(3000 scf bbl⁻¹) was maintained and hydrogen gas was vented without recycle. The reactor system was operated at steady state for 1 h prior to the period in which fuel product was collected.

Compositional analyses of the fuels was performed using low resolution mass spectrometry. The hydrocarbon group type compositions of the samples were determined by a modification of the method originally developed by Robinson (3). This method requires no separation of the sample into saturate and aromatic fractions. The aromatic carbon content was obtained by ¹³C NMR analysis using a Varian XL-200 spectrometer.

Cetane numbers of fuel product samples were determined by means of an engine test. Determinations were made with a standard Cooperative Fuels Research test engine using a constant compression ratio method.

RESULTS AND DISCUSSION

Effects of Secondary Hydrotreating on Fuel Product

Compositions

Table 2 presents examples of fuel product compositions from secondary hydrotreating and processing conditions. The compositional analysis of the feedstock is included as well as corresponding aromatic carbon contents (determined by ^{13}C NMR) and cetane numbers of the fuels. The processing conditions cover a wide range of temperatures and pressures and results indicate that a carefully chosen optimum temperature of 380°C is required as well as severe operating pressures, at least 14 MPa, to achieve the required diesel fuel ignition specification, i.e., cetane number 40. The optimum operating conditions coincide with those of previous work for upgrading middle distillates from delayed-coked bitumen (1).

Examination of the fuel compositions in Table 2 for various processing conditions shows some of the effects of temperature and pressure. It is noted that the concentrations of aromatics are affected by the shift of thermodynamic equilibrium. High temperatures and low pressures favour the formation of aromatics. These effects were discussed in detail previously (1).

At the optimum hydroprocessing conditions, the compositional analyses also show that, essentially, almost complete conversion of aromatics to naphthenes is required to produce specification diesel fuel. Thus experimental condition 3, producing fuel of cetane number 42.5, indicates only residual levels of benzocycloparaffins, benzodicycloparaffins and naphthalenes. The low 0.2% level of naphthalenes, may in fact be due to an intrinsic analytical error. Total saturates in the fuel is 98.8%.

Interrelation of Fuel Aromaticity with Cetane Number

Figure 1 shows plots of per cent aromatic carbon (% C_a) versus cetane number for fuel products from both distillates and shows the aromatic carbon contents and cetane numbers of both feedstocks with the current Canadian diesel fuel specification (cetane number 40, indicated by a broken line).

Figure 1 reveals qualitative differences between middle distillates from syncrudes A and B. For any aromatic carbon content, the syncrude produced by delayed coking of bitumen gives a distillate of superior cetane rating. Examination of the compositions of distillates from these syncrudes before and after secondary hydro-treating reveals that distillate from syncrude B is always significantly higher in paraffins and this almost certainly accounts for the better fuel ignition quality.

We attribute the curvatures of the plots in Figure 1 to the presence of various aromatic carbon types of different reactivities which determine their resistance to hydrogenation and combustion more or less equally. Thus, under relatively mild hydroprocessing conditions, a significant percentage of the total aromatic carbon content may easily be converted but this may have little effect on the fuel ignition quality. As processing severities are increased, more stable species are saturated but it appears that the largest gains in cetane improvement are made only after the greater portion of aromatic carbons are converted.

Figure 2 presents a plot of mass per cent total aromatics (% M_a) (determined on a molecular basis by mass spectrometry) versus cetane number. It is interesting to compare this with the corresponding plot for per cent aromatic carbon given in Figure 1. Figure 2 appears to be almost linear except for some curvature in the high cetane number area and it is apparent that we do not obtain the same degree of curvature found in Figure 1. The explanation for this phenomenon is that, when dealing with aromatic molecular species rather than aromatic carbons, we observe the effects of conversion of polynuclear aromatic compound types to their corresponding hydroaromatic forms during primary ring saturation. Thus, at low severities, conversion of one aromatic hydrocarbon group type to another maintains the overall total

molecular aromatic content. The true curvature of Figure 2 is better demonstrated by plotting the major aromatic hydrocarbon group types in the feed and products individually against cetane number. Table 2 shows that the predominant aromatic species are alkylbenzenes, benzocycloparaffins and benzodicycloparaffins. Figure 3 presents a plot of mass per cent versus cetane number for these species and shows that the curves approach zero values at different points. Again, recent work showed that at the optimum operating conditions the relative rates of hydrogenation of these species over sulfided Ni-W/ γ -Al₂O₃ are alkylbenzenes > benzocycloparaffins > benzodicycloparaffins, therefore relationships in Figure 3 should be linked to these findings (4). As noted above, at the optimum conditions, we observe that the conversion of alkylbenzenes is complete, but small amounts of the other two monoaromatic species continue to influence the cetane number beyond 41. Thus residual amounts of these components remain even after severe processing.

Correlation of Hydrogen Consumption with Cetane Number Improvement

Figure 4 presents a plot of hydrogen consumption versus the measured cetane number improvement. Values of Δ cetane number were obtained from the difference of values between product and feed as determined by engine test.

The plot is a smooth curve which intercepts the ordinate at approximately 25 m^3 (hydrogen) m^{-3} (feedstock). The apparent deviation of the intercept point from zero suggests that the input of low hydrogen levels into the feestock has no impact on cetane number. Such low conversions are achieved under mild processing conditions and our interpretation of this phenomenon is that we observe the partial saturation of compounds such as naphthalenes and naphthocycloparaffins to their corresponding hydroaromatic forms. It is expected that these conversions will affect only marginally the cetane rating.

For the syncrude A distillate Figure 4 shows that to raise the cetane number to the specification level of 40, i.e. by 9 points, an input of approximately 120 m^3 (hydrogen) m^{-3} (feedstock) (670 scf/bbl) is required.

SUMMARY

The diesel ignition properties of the fuels are found to be strongly related to the concentrations of aromatics as measured by two analytical techniques. In the case of aromatic carbon content, comparisons were made with previous results obtained for distillate from a synthetic crude produced by delayed coking of bitumen. These relations indicate that certain aromatic compounds may significantly retrograde the cetane rating of synthetic fuels even when present in small amounts, but more work would have to be done to confirm this.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the contributions of N. Kallio, NRC, Canada in the determination of cetane numbers.

LITERATURE CITED

1. Wilson, M.F. and Kriz, J.F., Fuel 1984, 63, 190.
2. Takematsu, T. and Parsons, B.I., Technical Bulletin TB187, Department of Energy, Mines and Resources, Ottawa, Canada, 1972.
3. Robinson, C.J., Anal. Chem. 1971, 43, 1425.
4. Wilson, M.F., Fisher, I.P. and Kriz, J.F., work submitted for publication.

TABLE 1

PROPERTIES OF MIDDLE DISTILLATE FEEDSTOCKS FROM ATHABASCA
SYNTHETIC CRUDES

	<u>Synthetic Crude A (fluid coked bitumen)</u>	<u>Synthetic Crude B (delayed coked bitumen)</u>
Relative density (15/15°C)	0.862	0.863
Carbon (wt%)	87.2	87.5
Hydrogen (wt%)	11.7	12.5
Sulphur (ppm)	97	550
Nitrogen (ppm)	37	54
Average molecular weight	200	201
% Aromatic carbon by ¹³ C n.m.r.	17.5	14.3
Cetane number (CCR method)	31	35
Distillation (D86)		
Initial b.p. °C	163	142
5%	183	
10%	192	181
20%	210	
50%	251	232
90%	296	283
Final b.p.	318	333

TABLE 2

EXAMPLES OF FUEL PRODUCT COMPOSITIONS FROM SYNTHETIC CRUDE A
BEFORE AND AFTER SECONDARY HYDROTREATING

	<u>Feedstock</u>	<u>Processing conditions and products</u>			
		1	2	3	4
	Middle distillate from synthetic crude A	300°C LHSV 0.75 3.55 MPa	300°C LHSV 0.75 7.00 MPa	380°C LHSV 0.75 17.3 MPa	420°C LHSV 0.75 17.3 MPa
Paraffins	15.8	18.3	17.8	19.5	21.0
Total cycloparaffins	42.4	45.5	57.3	79.3	75.5
Non-condensed monocycloparaffins	20.5	22.5	26.4	39.2	38.3
Condensed dicycloparaffins	14.4	16.3	21.3	28.3	25.1
Condensed polycycloparaffins	7.5	6.7	9.5	11.8	9.1
Total aromatics	41.9	36.3	24.9	1.3	6.2
Alkylbenzenes	17.3	17.8	11.4	-	1.7
Benzocycloparaffins	12.9	13.4	9.4	0.5	3.1
Benzodicycloparaffins	5.2	3.6	2.9	0.6	1.4
Naphthalenes	3.5	1.0	0.6	0.2	0.3
Naphthocycloparaffins	1.6	0.1	-	-	-
Fluorenes	1.0	0.4	0.5	-	-
Triaromatics	0.4	-	-	-	-
% Aromatic carbon (¹³ C NMR)	17.5	14.5	9.0	0.8	3.2
Cetane number (CCR method)	31	32.4	35.2	42.5	38.6

FIGURE CAPTIONS

1. Per cent aromatic carbon (^{13}C NMR) vs. cetane number for hydrotreated distillates from synthetic crudes A and B.
2. Mass per cent total aromatics vs. cetane number for hydrotreated distillate from synthetic crude A.
3. Mass per cent of monoaromatic species vs. cetane number for hydrotreated distillate from synthetic crude A.
4. Correlation of hydrogen consumption with cetane number improvement for hydrotreating distillate from synthetic crude A.

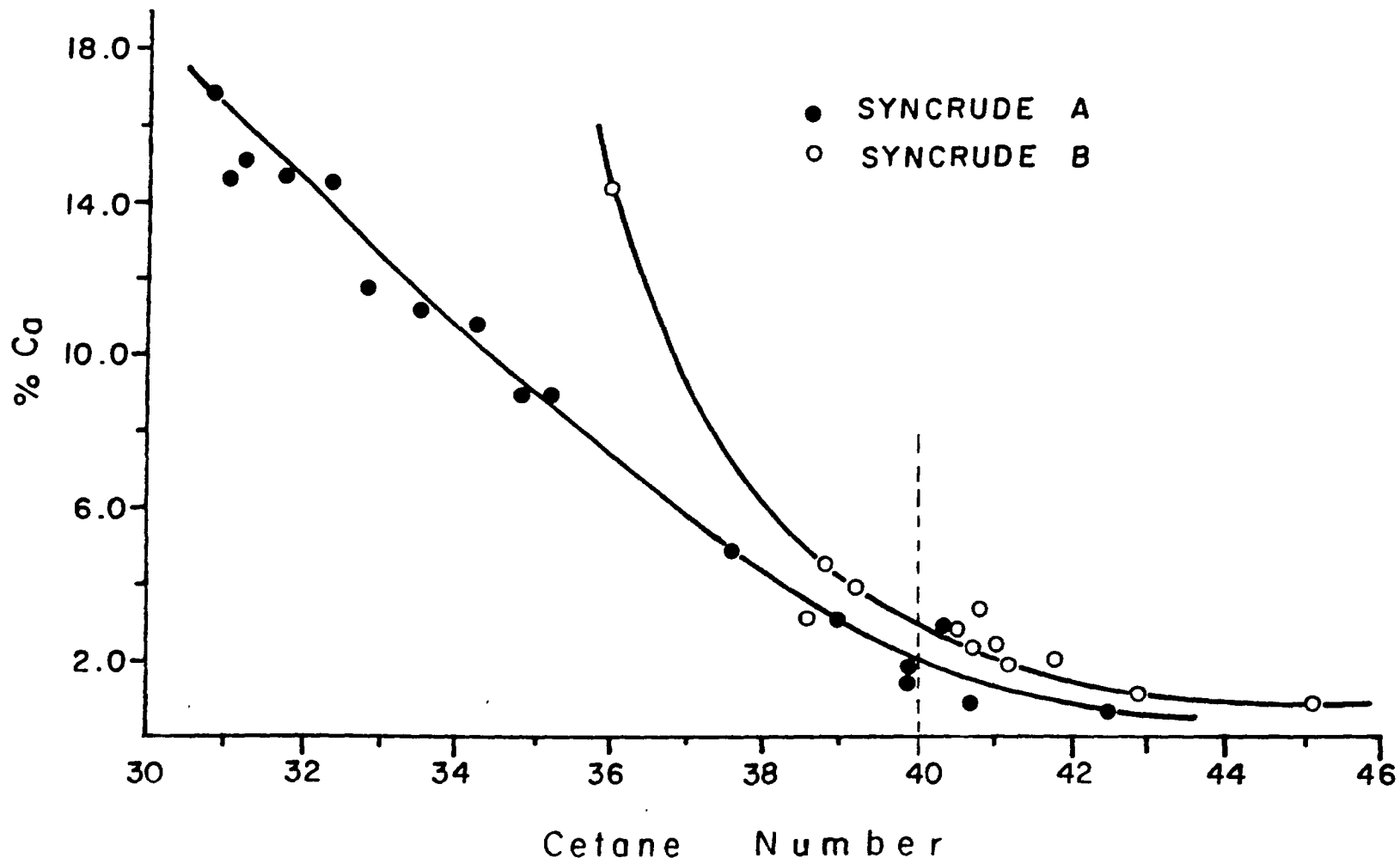


FIG. 1

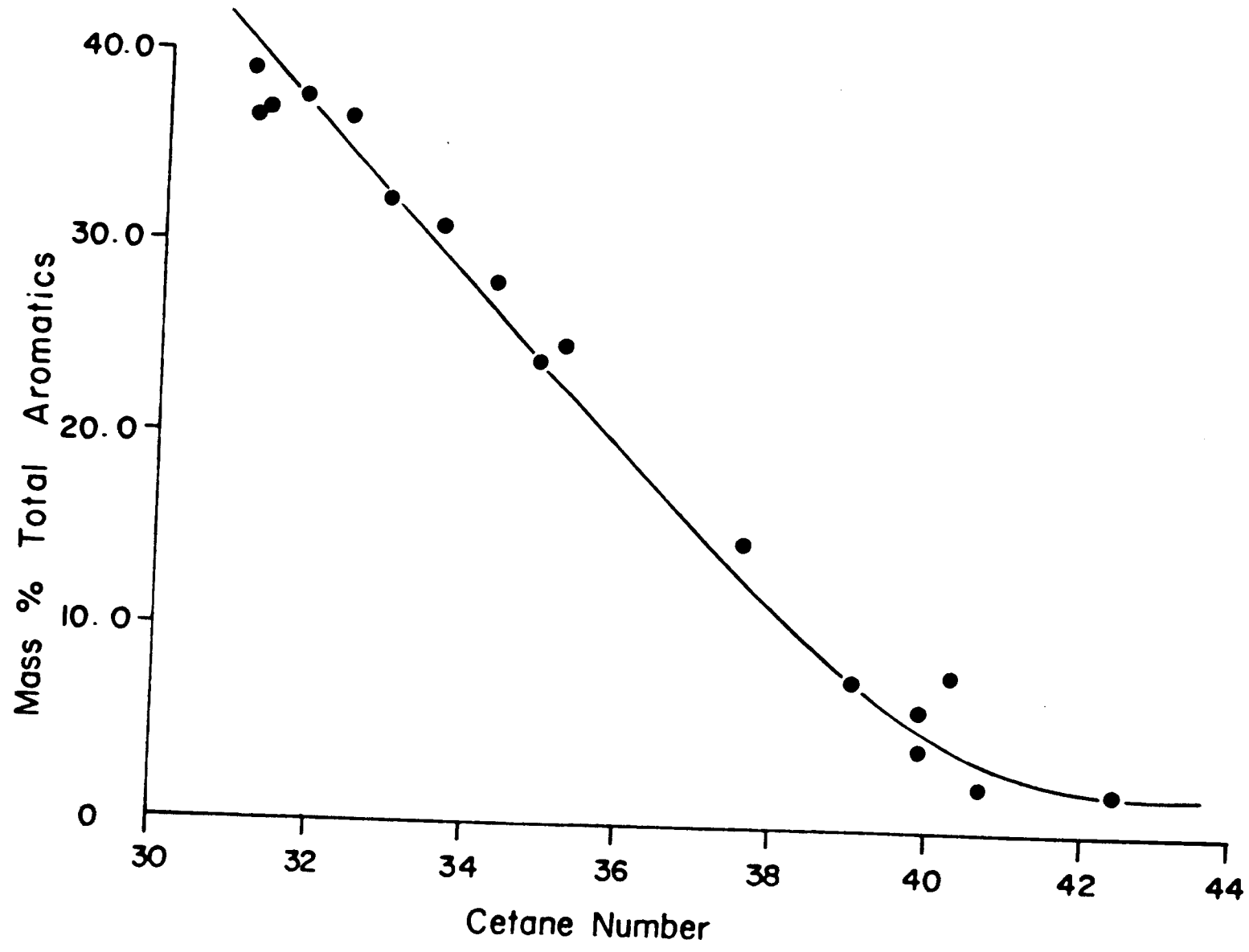


FIG. 2

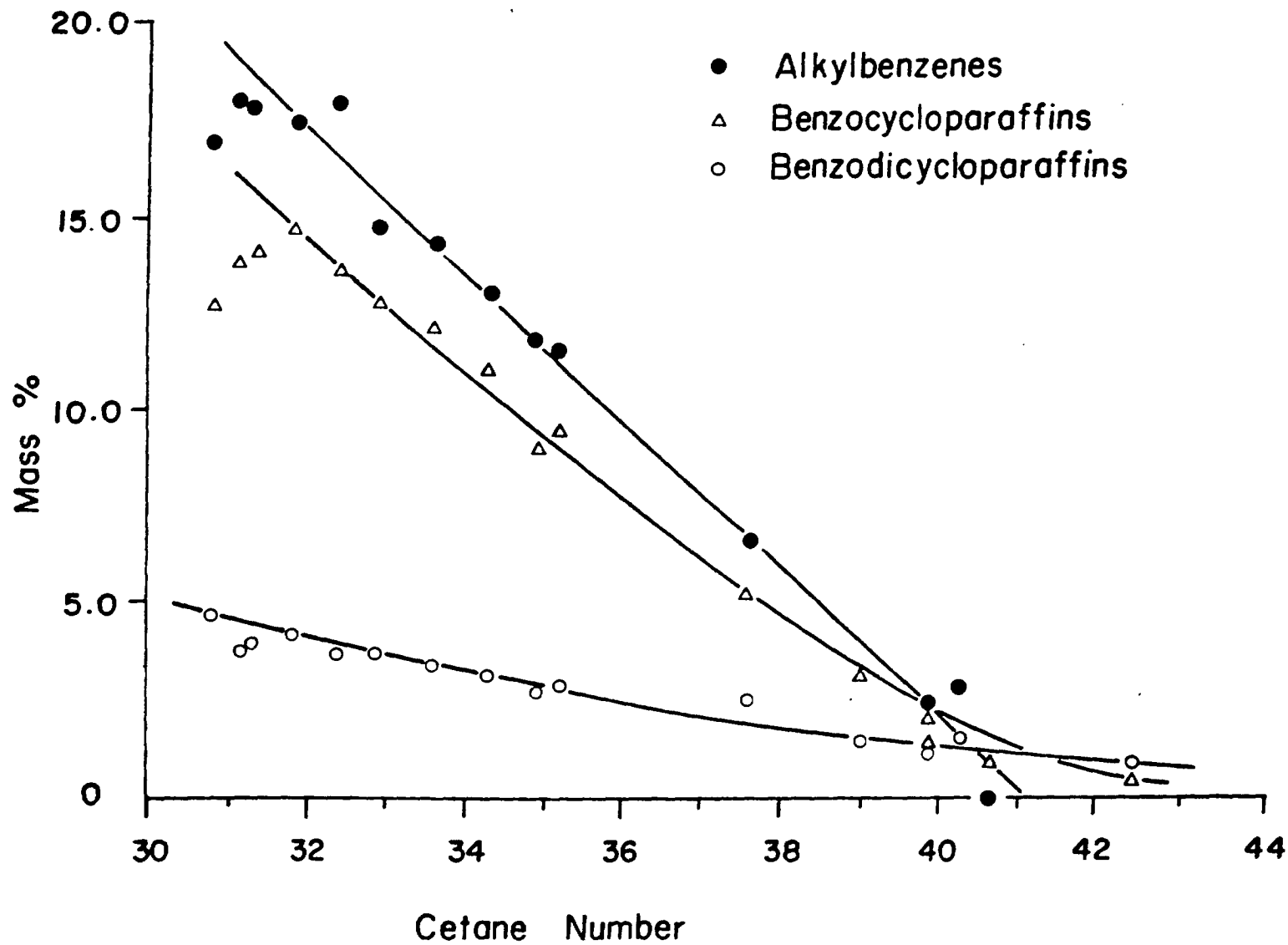


FIG. 3

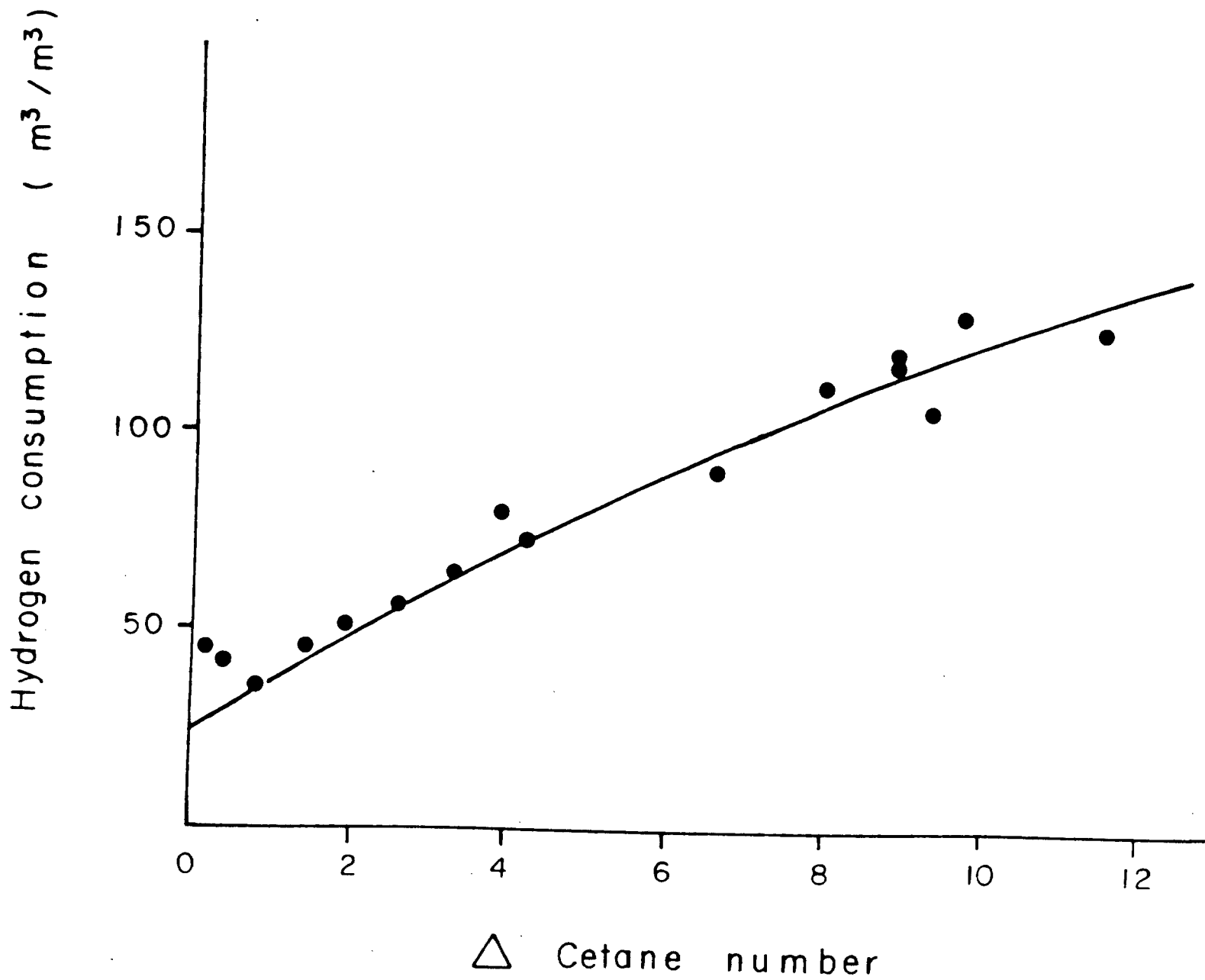


FIG. 4