

Fischer-Tropsch Synthesis in Slurry-Reactor Systems

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Department of Chemical Engineering  
and  
Energy Laboratory  
Massachusetts Institute of Technology  
Cambridge, Massachusetts

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Submitted by:

C.N. Satterfield

T. Bartos

H. Stenger

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## I. SUMMARY

Professor Satterfield presented a paper, co-authored with G.A. Huff, Jr., entitled, "Mass Transfer and Product Selectivity in a Mechanically-Stirred Fischer-Tropsch Slurry Reactor," at the Seventh International Symposium on Chemical Reaction Engineering (ISCRE-7) held in Boston on October 4-6, 1982. The paper is published in the symposium proceedings, A.C.S. Symposium Series #196, 225-226. We also were hosts to a considerable number of attendees at ISCRE-7 from the U.S. and abroad who wished to visit our laboratories and discuss various aspects of Fischer-Tropsch synthesis. Prof. Satterfield also presented a summary of recent accomplishments under this grant at a D.O.F. Contractor's Conference in Pittsburgh during September 1982.

An Mn/Fe catalyst prepared at the Technical University of Berlin was studied under a set of conditions chosen to compare the results with a reduced fused magnetite catalyst and with a similar catalyst studied by Deckwer et al. (I.E.C. Proc. Des. Dev., 21, 222 (1982)). The results are presented in the form of a manuscript attached herewith that has been submitted to the same journal for publication.

The pattern of product selectivity with the Mn/Fe catalyst was very similar to that observed with a reduced fused magnetite catalyst in the same apparatus, but the olefin/paraffin ratio at all carbon numbers was less than that with the reduced magnetite catalyst. With both catalysts the Flory-Schultz distribution was followed but two values of the chain growth probability,  $\alpha$ , were found, with a sharp discontinuity at about  $C_{11}$ .  $\alpha$  values based on the  $C_1$ - $C_{10}$  products were less for the Mn/Fe catalyst than for the fused Fe catalyst, attributed to the absence of potassium in the

Mn/Fe catalyst. The activity of the present Mn/Fe catalyst was moderately less than that reported for a similar catalyst studied by Deckwer in a bubble column.

#### FUTURE WORK

A two-week delay has been incurred in our experimental program due to the failure of a Research Control Valve used to control the inlet synthesis gas flow. While the valve is being repaired, the opportunity has been taken to give preventive maintenance to all our analytical equipment, leak test and clean all of our downstream product lines, and check the calibrations on our gas chromatograph. When back on stream we intend to study a second Fe/Mn catalyst, prepared and made available by Richard Diffenbach of P.E.T.C.

Fischer-Tropsch Synthesis  
on a Precipitated Mn/Fe Catalyst  
in a Well-Mixed Slurry Reactor

Charles N. Satterfield

and

Harvey G. Stenger

Department of Chemical Engineering  
Massachusetts Institute of Technology  
Cambridge, MA 02139

Abstract

The pattern of product selectivity was very similar to that observed with a reduced fused magnetite catalyst in the same apparatus, but the olefin/paraffin ratio at all carbon numbers was less than that with the reduced magnetite catalyst. With both catalysts the Flory-Schultz distribution was followed but two values of the chain growth probability,  $\alpha$ , were found, with a sharp discontinuity at about  $C_{11}$ .  $\alpha$  values based on the  $C_1$ - $C_{10}$  products were less for the Mn/Fe catalyst than for the fused Fe catalyst, attributed to the absence of potassium in the Mn/Fe catalyst. The activity of the present Mn/Fe catalyst was moderately less than that reported for a similar catalyst studied elsewhere in a bubble column.

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Patents by Kölbel and Tillmetz (1) and Busseneier et al. (2)

claimed that certain manganese-iron catalysts of low Fe/Mn ratio had unusual selectivity for olefins and suggested that the products did not follow the Schulz-Flory distribution. These claims have been recently disputed by Deckwer et al. (3) and van Dijk et al. (4). Deckwer et al. studied a Mn/Fe catalyst in a bubble column reactor at 282 to 303°C and about the same product distribution was obtained as in fixed bed studies with the same catalyst. In this respect their results also differed from a report by Kölbel et al. (5) that significant differences in the C<sub>1</sub> to C<sub>4</sub> product distribution occurred between fixed and slurry phase operation, using a similar Mn/Fe catalyst. Van Dijk et al. reported on a briefer study of a Mn/Fe catalyst in a fixed bed reactor combined with characterization of the catalyst by Mossbauer spectroscopy and X-ray diffraction. For comparison with the study of Deckwer et al., we report here a limited study on a precipitated Mn/Fe catalyst in a mechanically-stirred reactor described elsewhere (6). Because of the excellent mixing the reactor contents are uniform in composition, which simplifies interpretation of results.

#### EXPERIMENTAL

The Mn/Fe catalyst was prepared by Dr. H.-J. Lehmann at the Technical University of Berlin, about January 1980, by their continuous precipitation method. It is presumably essentially the same as that studied by Deckwer et al. It analyzed 8.06% Fe, 58.28% Mn and 33.72 wt% O (Galbraith Labs). It was pretreated in the identical manner as that outlined by Deckwer et al. and

reaction conditions were chosen to allow as nearly direct comparison as possible with Deckwer's results and with our studies in the same apparatus of a K-promoted reduced fused magnetite catalyst. The Mn/Fe catalyst is stated by Deckwer to be a mixture of Fe compounds (magnetite, carbides) and MnO.

52.8 gm of the Mn/Fe catalyst was added to 400 gm of n-octacosane in the reactor. For activation helium was first passed through the slurry while it was heated up and then CO alone was passed through the slurry for 24 hours, followed by H<sub>2</sub> alone for 24 hours. For all three gases, conditions were 0.65 L/min, 0.78 MPa, and 260°C.

#### RESULTS AND DISCUSSION

Reaction was carried out at 283°C, 1.24 MPa with an inlet H<sub>2</sub>/CO ratio of 1.19 and a gas flow rate of 0.70 L/min (at 25°C and 1 atm). Steady-state activity was obtained after 12 hours and was maintained for the further 60 hours of the run. During the first 400 minutes gas samples were taken at various intervals and analyzed for C<sub>1</sub> to C<sub>5</sub> hydrocarbons to indicate some of the trends in product composition during start-up. Over the last 30 hours a complete product sample of liquids and gas was collected and used for the steady state results presented here. Further studies were not possible because of equipment malfunction. The material balance on total weight for the steady-state samples, including water formed, closed at 97.4%. At steady state 13.3% of the H<sub>2</sub> and 18.0% of the CO was converted and exit partial pressures, which are the same as those throughout the reactor, were  $P_{CO} = 0.51$  MPa and  $P_{H_2} = 0.65$  MPa.

### Startup

Activity: During the initial reaction period the activity of the Mn/Fe catalyst of van Dijk et al., studied at 240°C, increased to a maximum at about 1 1/2 hours and then decreased to a nearly constant level, equal to about 1/2 of the maximum, at about 20 hours when the run was concluded. With the present catalyst, the first activity measurement was at 50 minutes, after which the activity dropped to a steady-state level about 20% below that first observed (Fig. 1). During the 20 hour run described, van Dijk et al. reported a steady increase in the ethylene/ethane ratio. The present Mn/Fe catalyst showed similar behaviour as followed during the first 400 minutes. Figure 2 presents data on the mole fraction of olefin species of carbon number n present in the total of C<sub>1</sub> through C<sub>5</sub> gas phase products. For each C number the fraction present as olefins increased with time; the C<sub>2</sub>H<sub>4</sub> concentrations were low, as usual. Figure 3 presents similar data for paraffins. The usage ratio, defined as moles of H<sub>2</sub> converted per mole of CO converted, is shown in Figure 4 to increase from 0.8 to just over 1.0 during this time. This increase is probably a result of a loss in water gas shift activity. The equilibrium constant for this reaction is 50 at 283°C but, as shown on Figure 5, the ratio  $\frac{P_{H_2} \cdot P_{CO_2}}{P_{H_2O} \cdot P_{CO}}$  was substantially below equilibrium throughout the startup period and indeed decreased with time.

### Steady State

The results can be compared to our own previous studies with a reduced fused magnetite catalyst and with the results of Deckwer et al. of their Mn/Fe catalyst in their bubble column.

Activity: For iron catalysts in general the rate of consumption of CO plus H<sub>2</sub> is first order in H<sub>2</sub> and zero order in CO up to 60% conversion or more. For calculation of activity we determine a rate constant by the expression  $r_{\text{CO}+\text{H}_2} = k_0 m_{\text{C}} P_{\text{H}_2}$ , where the rate is consumption of moles of H<sub>2</sub> + CO per minute,  $m_{\text{C}}$  is gm of iron present in the catalyst, as iron, and  $P_{\text{H}_2}$  is in atmospheres.  $k_0$  therefore has the units moles/min·g Fe·atm H<sub>2</sub>.

Deckwer et al. reported activity data for four different inlet CO/H<sub>2</sub> ratios. Most of their runs were at or near a ratio of 1.7. This ratio provided the highest rate of reaction and it was only for these runs that consistent rate constants could be evaluated by Deckwer et al. The activity of the catalysts dropped with CO/H<sub>2</sub> inlet ratio in the order: 1.73 > 1.35 > 2.29 > 0.73 and they suggested that hydrogen-rich gases give anomalous results. However, such an irregular pattern is odd and we note that the above is also the order in which runs were made. This suggests to us that the catalyst was deactivating with time and it was this effect rather than an effect of CO/H<sub>2</sub> ratio that was being observed. For their most active conditions, we calculate that their Mn/Fe catalyst had at 283°C a value of  $k_0 = 8.0 \times 10^{-4}$ , based on the correlation in their Fig. 12. For a study by Mohammed quoted by Deckwer, at 300°C, we calculate that  $k_0 = 1.6 \times 10^{-4}$ . However this catalyst was prepared by an earlier batch-type procedure that Deckwer et al. state does not give reproducible results.

From the study of our Mn/Fe catalyst we calculate  $k_0 = 1.5 \times 10^{-4}$  at 282°C. From data on our fused iron catalyst at 263°C (7),



extrapolated to 282°C with an activation energy of 79 kJ/mole, we calculate  $k_0 = 5.8 \times 10^{-4}$ . This basis of comparison is, of course, not entirely valid, since such factors as surface area are not considered.

Selectivity: Our method of product analysis allows us to determine for each carbon number, the mole fraction present of n-paraffins,  $\alpha$  and  $\beta$  n-olefins (these are mostly  $\alpha$ ), oxygenates, and a "remainder" that consists primarily of branched hydrocarbons, both paraffinic and olefinic, plus a small fraction of cyclic compounds. The product distribution plot of Figure 6 shows a great similarity to those obtained with a reduced fused magnetite catalyst (7). With both catalysts a Schultz-Flory plot of the total organic products (sum of all four categories) breaks sharply at about  $C_{11}$ , while the olefin and oxygenate distributions are continuous. However the chain growth probability,  $\alpha$ , based on total organic production, is 0.55 and 0.75, respectively, for the low and high carbon numbers, for the Mn/Fe catalyst in contrast to about 0.7 and 0.93 for the fused iron catalyst. Deckwer et al. reported  $\alpha = .67$  for  $C_1-C_{16}$  (see below).

Interpretation of the double  $\alpha$  is discussed elsewhere. The values of  $\alpha$  here (based on the  $C_1-C_{12}$  fraction) may be rationalized as follows:

(1) It is known that the presence of K in an iron catalyst increases  $\alpha$ .

(2) In studies with the fused iron catalyst we found that feeding higher ratios of  $H_2/CO$  to the reactor resulted in a product

distribution corresponding to a lower  $\alpha$ , although the effect was fairly small. This is presumably an effect of the overall stoichiometry on catalyst surface composition. Assuming that the same effects occur with Mn/Fe, the lower  $\alpha$  of our Mn/Fe catalyst compared to that of Deckwer can possibly be attributed to our  $(\text{H}_2/\text{CO})_{\text{in}}$  of 1.19 versus  $(\text{H}_2/\text{CO})_{\text{in}} = 0.6$  for Deckwer et al. The higher  $\alpha$  of 0.7 for our fused iron catalyst is attributed primarily to the presence of K, being slightly compensated for by the  $(\text{H}_2/\text{CO})_{\text{in}}$  of 1.81.

Figure 7 is a comparison at each carbon number of the olefin selectivity observed with the fused iron catalyst versus that with the manganese/iron catalyst. At each carbon number the olefin/paraffin ratio is higher for the fused iron catalyst than for the Mn/Fe catalyst and the ratio drops with C number more rapidly with the Mn/Fe catalyst than for the fused iron catalyst. The fused iron catalyst was much more active than the Mn/Fe catalyst on a total weight basis and we cannot match conditions precisely. For comparison, we chose a fused iron study at the highest temperature and about the same hydrogen pressure. This was 263°C, 1.46 MPa total pressure,  $(\text{H}_2/\text{CO})_{\text{in}} = 1.81$ . Conversion of hydrogen plus carbon monoxide was about 54% and the exit gas composition (which equals that throughout the reactor) was  $P_{\text{H}_2} = 0.80$  MPa and  $P_{\text{CO}} = 0.20$  MPa. For the Mn/Fe catalyst  $(\text{H}_2/\text{CO})_{\text{in}} = 1.19$ , conversion was 15% and exit gas composition was  $P_{\text{H}_2} = 0.65$  MPa and  $P_{\text{CO}} = 0.51$  MPa. With the fused iron catalyst we found little effect of degree of conversion on olefin/paraffin ratio for  $\text{C}_3^+$  products for

certain runs in which the partial pressure of hydrogen remained essentially constant with varying conversion. However, this ratio increased with decreased hydrogen partial pressure in the system and with increased temperature, and was essentially independent of CO or CO<sub>2</sub> partial pressure. If the same trends of pressure and temperature were to have the same effect with the Mn/Fe catalyst, the ratio would be expected to be greater here than that for the fused iron rather than less.

Deckwer et al. reported an O/P ratio of 4 to 5.5 for the C<sub>3</sub> fraction versus 2.5 here and 1.7 to 2.7 for the normal C<sub>4</sub> fraction versus 4 here, for studies at 293 to 298°C, (H<sub>2</sub>/CO)<sub>in</sub> of 0.62 or 0.60 and 30 to 44% conversion. Their runs at (H<sub>2</sub>/CO)<sub>in</sub> of about 0.6 gave a good Schulz-Flory distribution, based on hydrocarbon products from CH<sub>4</sub> through C<sub>12</sub>, C<sub>2</sub> being low as usual. With (H<sub>2</sub>/CO)<sub>in</sub> of 1.37, CH<sub>4</sub> production increased greatly and the O/P ratio of the C<sub>2</sub>-C<sub>4</sub> fraction greatly dropped. However, with our value of (H<sub>2</sub>/CO)<sub>in</sub> of 1.19 (and 1.27 out) we obtain a good Schulz-Flory distribution, including CH<sub>4</sub>. We thus suggest that the markedly different behaviour of the Deckwer catalyst at (H<sub>2</sub>/CO)<sub>in</sub> of 1.37 may have been caused not by the (H<sub>2</sub>/CO) ratio but by the immediately-preceding run being carried out at a (H<sub>2</sub>/CO)<sub>in</sub> of 0.44. This could have drastically altered the catalyst composition.

#### ACKNOWLEDGMENT

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FIGURE CAPTIONS

- Figure 1 Activity decreases with time during start-up.
- Figure 2 Mole fraction of olefin of carbon number  $n$  present in total  $C_1-C_5$  gas phase increased during start-up.
- Figure 3 Mole fraction of paraffin of carbon number  $n$  present in total  $C_1-C_5$  gas phase decreased during start-up.
- Figure 4  $(H_2/CO)$  usage ratio increases with time during start-up.
- Figure 5 Activity for water-gas shift decreases with time during start-up.
- Figure 6 Steady-state distribution of products by carbon number.
- Figure 7 Mole ratio of  $n$ -olefins/ $n$ -paraffins as a function of carbon number for reduced fused magnetite and for Mn/Fe.

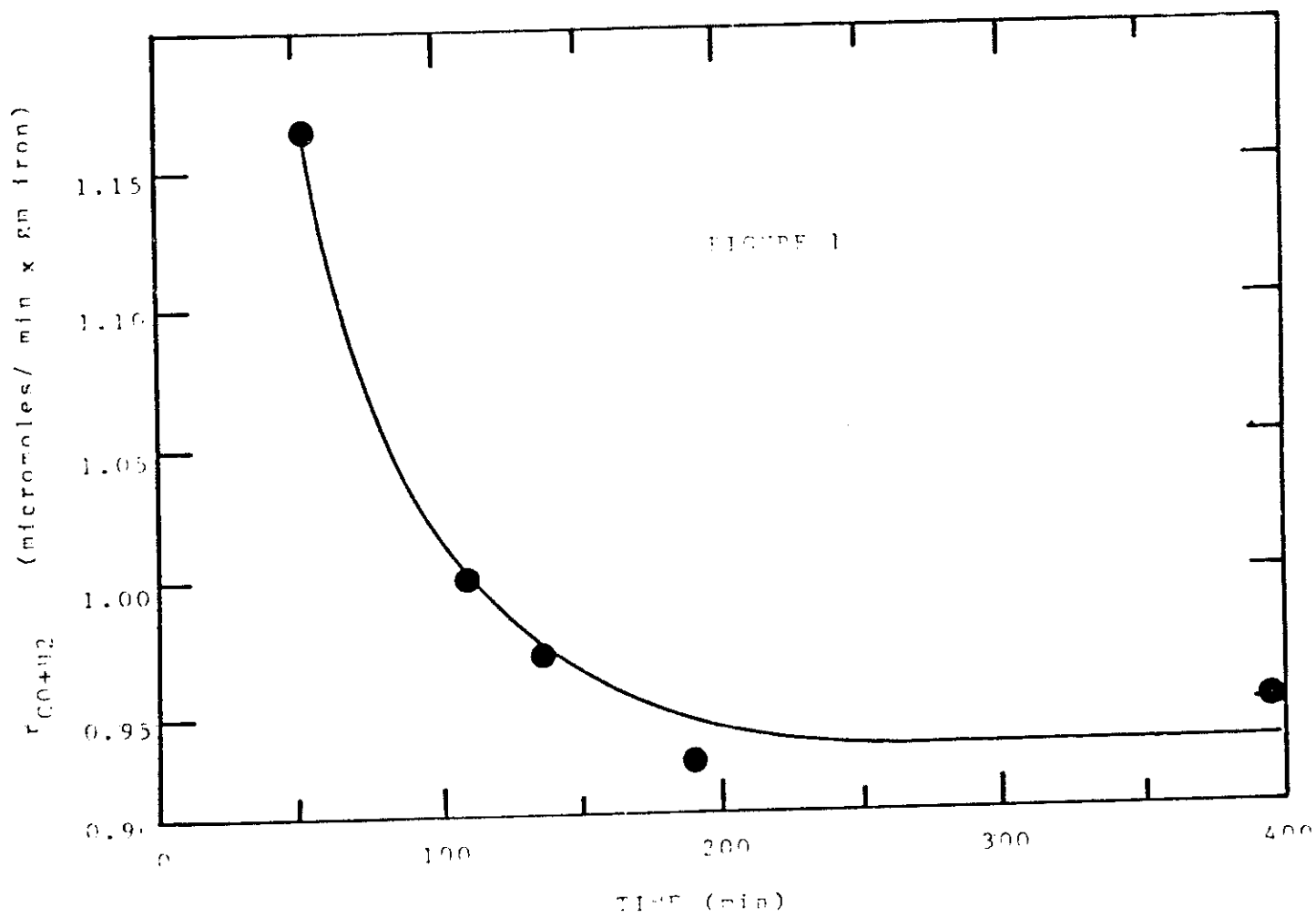


FIG. 1

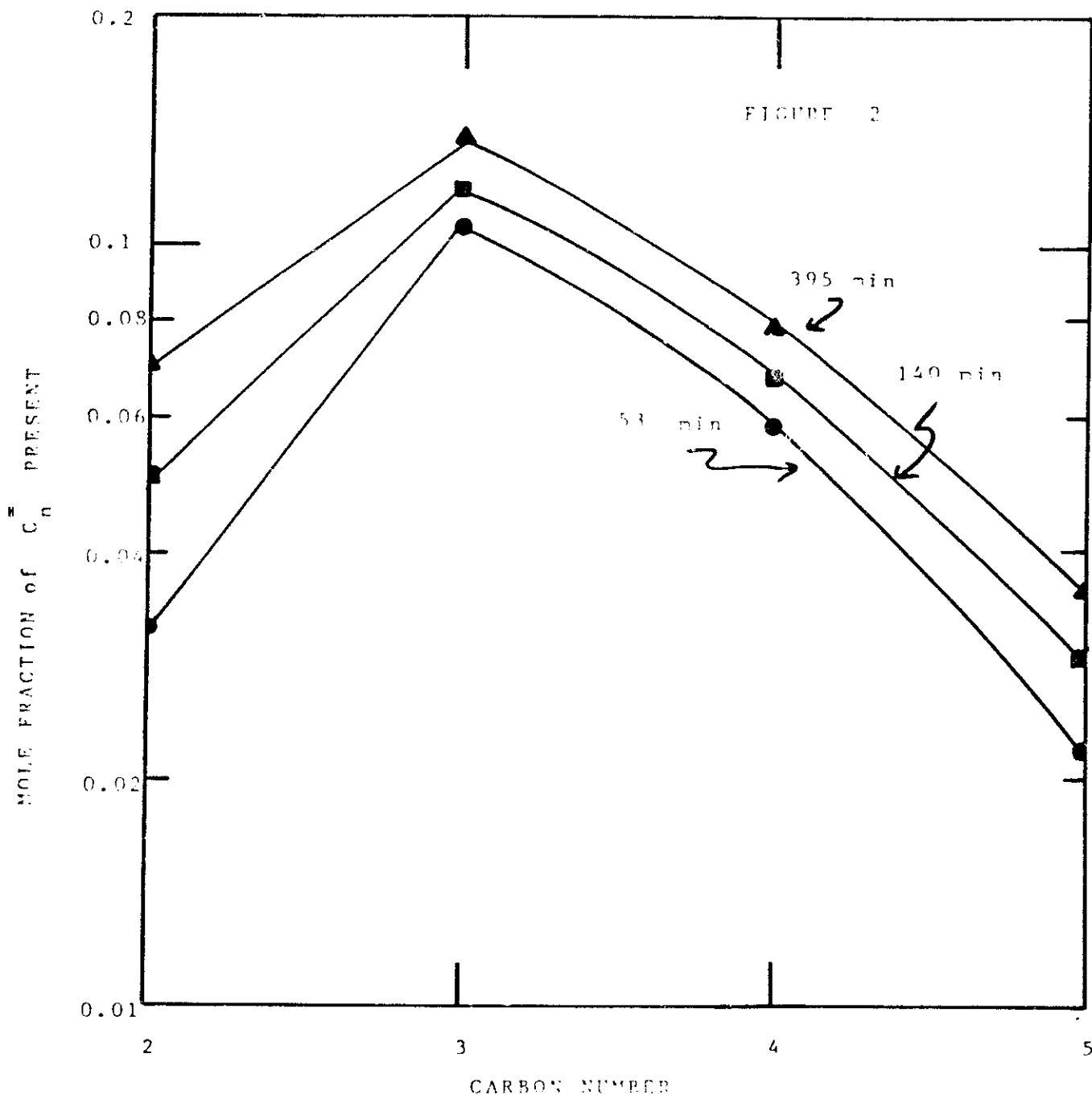


FIG. 2

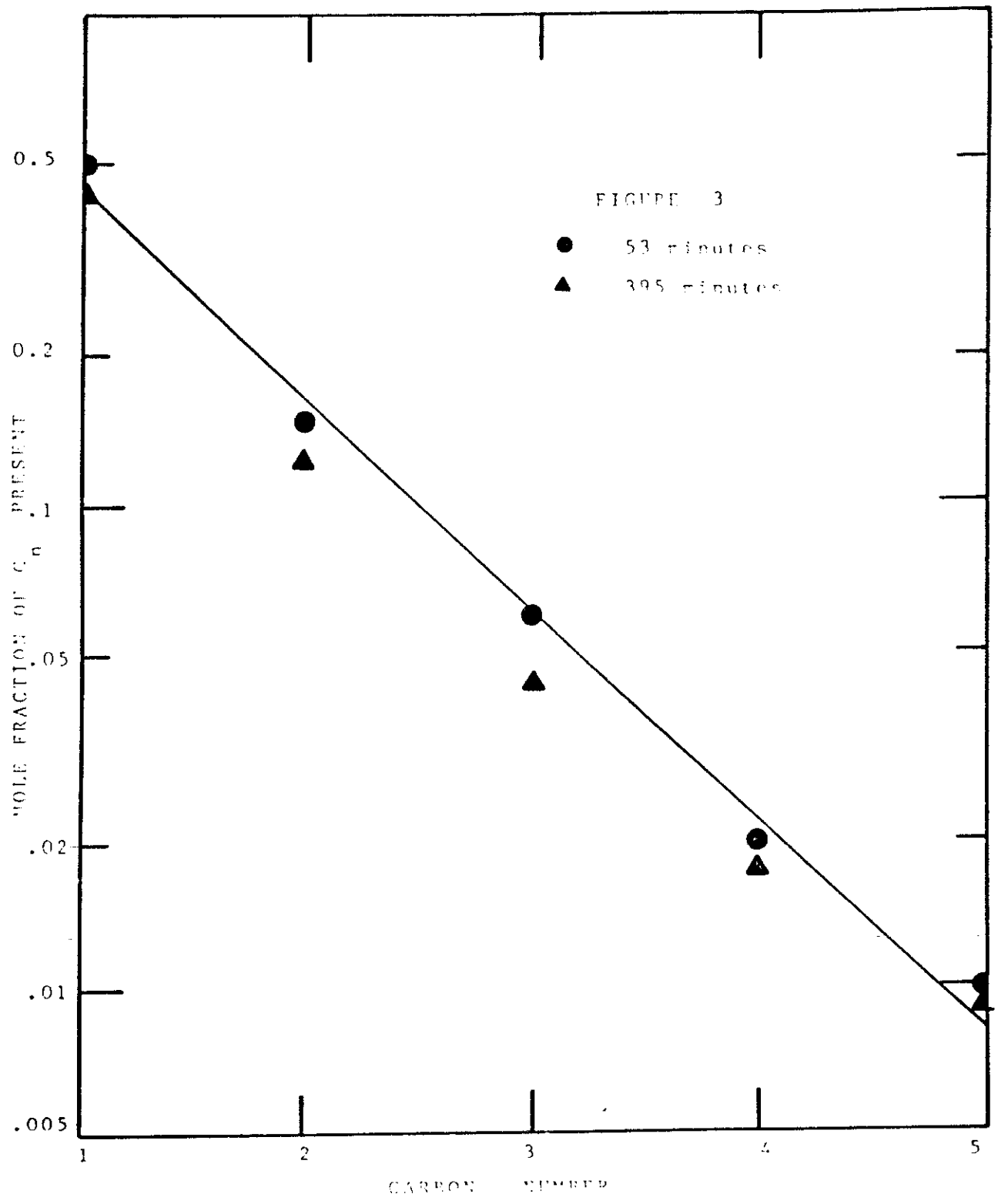


FIG. 3



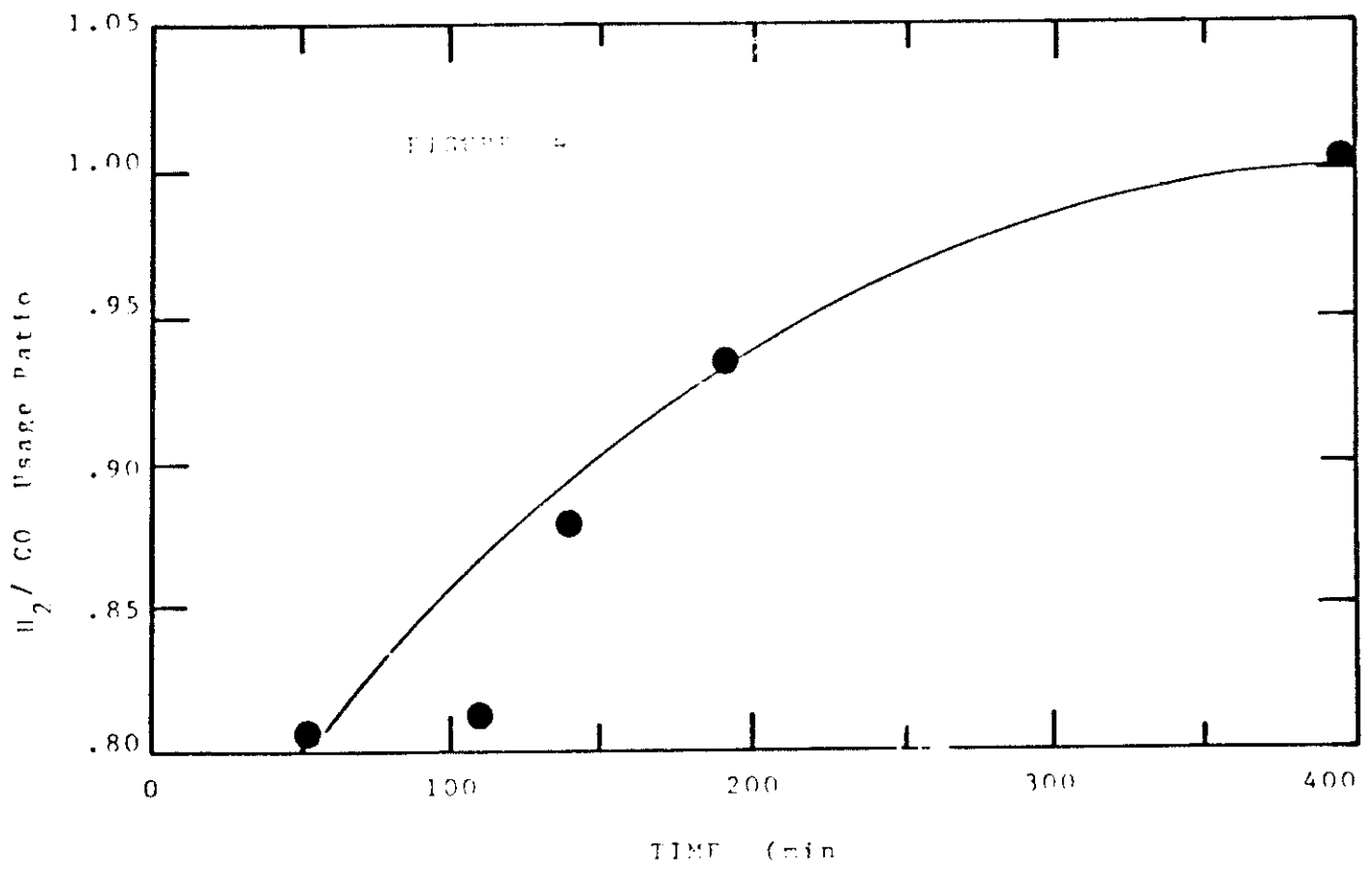


FIG. 4

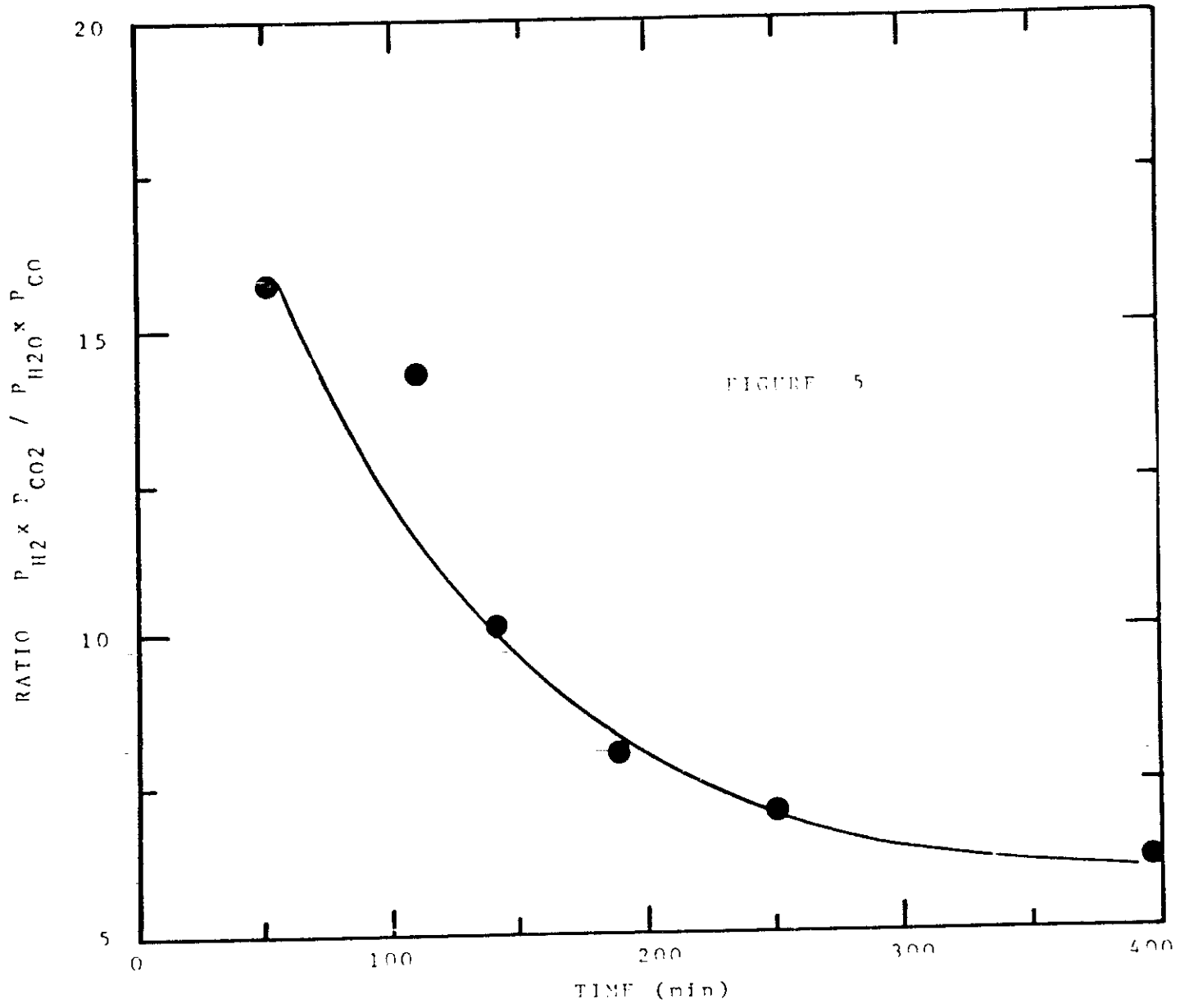


FIG. 5

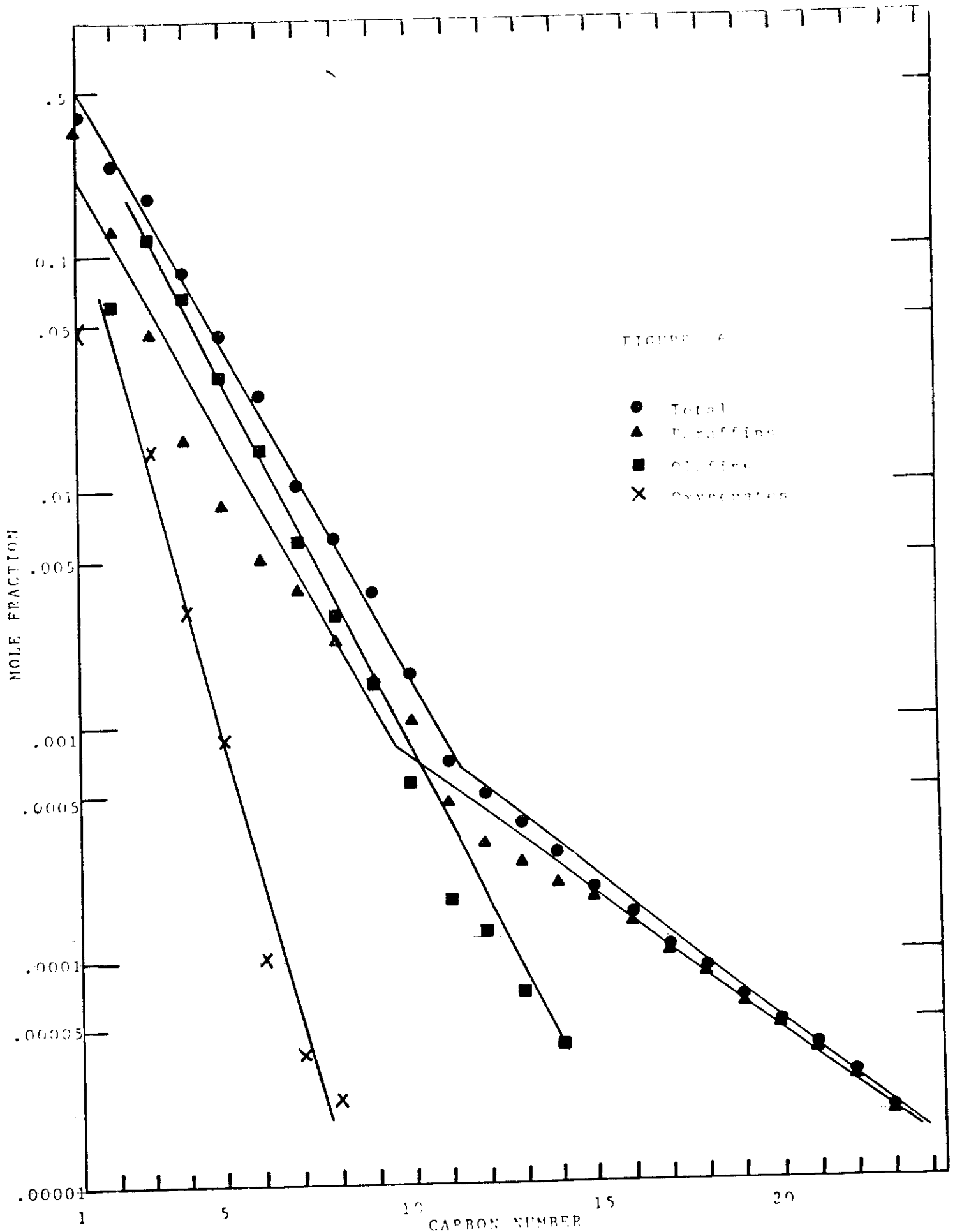


FIG 6

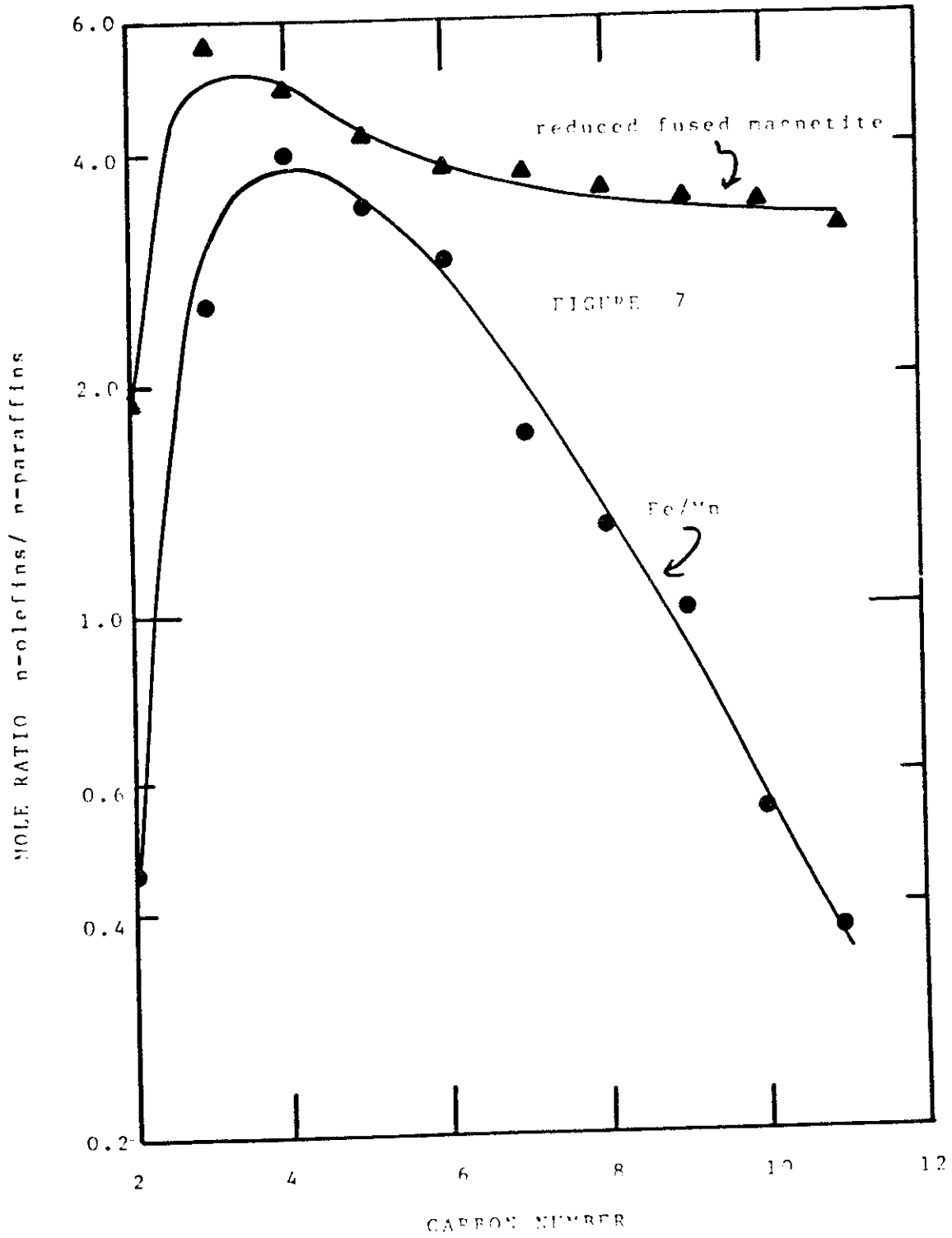


FIG. 7