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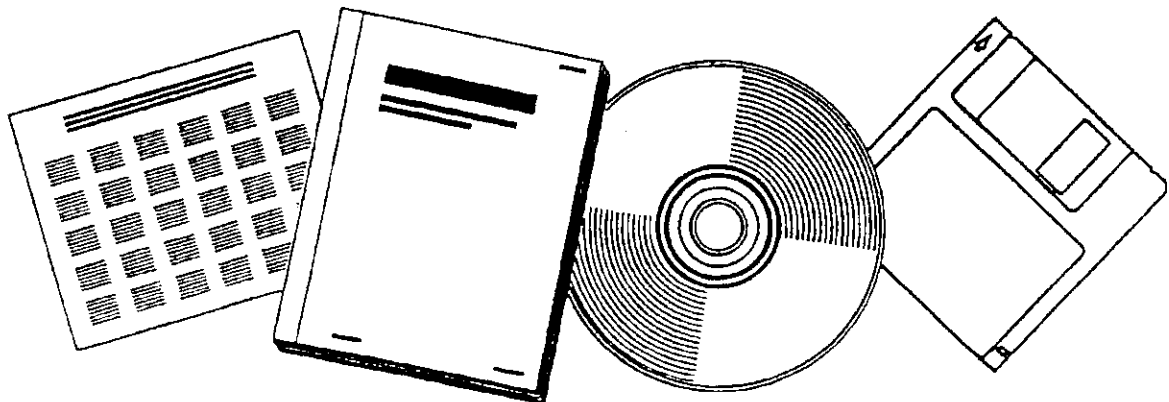
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**FISCHER-TROPSCH SYNTHESIS IN SLURRY
REACTOR SYSTEMS. QUARTERLY REPORT, AUGUST
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Fischer-Tropsch Synthesis in Slurry Reactor Systems

Quarterly Report for Period

August 1, 1983 to October 31, 1983

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Massachusetts Institute of Technology

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I. SUMMARY

During this quarter Prof. Satterfield presented a talk at a D.O.E. Contractors' Conference on Indirect Liquefaction at P.E.T.C. and Harvey Stenger presented a talk at a University Coal Research and AR & TD Liquefaction Contractors' Conference, also at P.E.T.C. We were also host, for discussions on Fischer-Tropsch synthesis, to Prof. Hans Schulz of the Engler-Bunte-Institut, University of Karlsruhe, Federal Republic of Germany; Dr. Mark Dry, of Sasol, South Africa and Prof. Komiyama, University of Tokyo, Japan.

In the Quarterly Report for November 1, 1982 to January 31, 1983 we presented a new and improved kinetic expression for the Fischer-Tropsch synthesis on an iron catalyst and suggested its use for kinetic modeling where information on a specific iron catalyst of interest was unavailable or inadequate. In the past it has usually been assumed that the reaction is first order in hydrogen and zero order in carbon monoxide, although it is known that this is inadequate at high conversions. We have now prepared a brief report, copy attached, which shows the extent to which the simple first-order expression will be in error as a function of degree of conversion and other variables. The effect of conversion on H_2/CO usage ratio is also presented.

In 1980 we analyzed several studies of Fischer-Tropsch synthesis in slurry bubble column reactors to estimate the degree of mass transfer resistance that may have been present (Satterfield and Huff, Chem. Eng. Sci., 35, 195 (1980)). Our analysis was subsequently discussed by Deckwer et al. (Chem. Eng. Sci., 36, 765, 791 (1981)) with a rejoinder from us (Chem. Eng. Sci., 36, 790 (1981)). The

subject continues to excite interest and further correspondence from Bukur and Gaupte of Mobil and van Vuuren of CSIR, South Africa, was recently published (Chem. Eng. Sci. 38, 1363, 1365 (1983)). A copy of our reply (Chem. Eng. Sci. 38, 1367 (1983)) is attached to this report. *Removed EKB*

Our extensive series of studies comparing the Fischer-Tropsch reaction in the presence of octacosane and in phenanthrene is still being analyzed. Some of the early work was affected by small amounts of a sulfur compound in the phenanthrene used. These studies were subsequently repeated with a highly-purified phenanthrene. The nature of the liquid clearly has an effect on the reaction that may be related at least in part to the increased solubility of H₂ and CO in phenanthrene.

COMMUNICATIONS

SOME KINETIC DESIGN CONSIDERATIONS IN THE FISCHER-TROPSCH SYNTHESIS ON A REDUCED FUSED-MAGNETITE CATALYST

Abstract

The results of calculations, based on a newly-developed kinetic model, show here the extent to which the simple first-order kinetic expression commonly used will be in error, as a function of degree of conversion and other variables. The effect of conversion on H_2/CO usage ratio is also presented.

Introduction

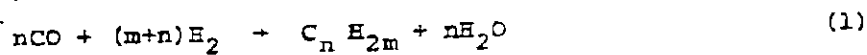
In recent proposed models for the Fischer-Tropsch synthesis in slurry reactors or bubble columns (Satterfield and Huff, 1980; Deckwer et al., 1981, 1982), the rate of synthesis gas consumption has generally been taken to be dependent only on the hydrogen concentration to the first power, based on Anderson's report (1956) that this was valid for synthesis-gas conversions below about 60%. Although it has been known that at higher conversions the rate is inhibited by CO and H_2O , the paucity of quantitative information has militated against trying to incorporate a more accurate, kinetic expression into such models.

We (Huff and Satterfield, 1983) recently conducted a systematic kinetic study on a reduced fused-magnetite catalyst in a well-stirred slurry reactor over a wide range of reaction conditions. Based on those results we have calculated and present here graphs showing sets of conditions for which the simple first-order expression is adequate and the extent to which this assumption

is in error as higher degrees of conversion are encountered. In previous modeling it has also been generally assumed that the (H₂/CO) usage ratio was independent of conversion. The adequacy of this assumption is also analyzed.

Chemistry of the Process

In general, the stoichiometry for the Fischer-Tropsch reaction may be expressed as:



In our kinetic study the average organic product composition was "C₃H₇", i.e. n = 3 and m = 3.5 in Eq. (1) (Satterfield and Huff, 1982).

Huff and Satterfield (1983) measured the rate of carbon monoxide plus hydrogen conversion (-R_{H₂+CO}) in a semi-continuous slurry reactor at 232 to 263°C, 445 to 1480 kPa, H₂/CO feed ratios of 0.55 to 1.8, hydrogen conversions of 17 to 68%, and carbon monoxide conversions of 16 to 98%. They quantitatively determined the inhibiting effects of carbon monoxide and water and proposed the following rate expression:

$$-R_{\text{H}_2+\text{CO}} = ab' \frac{P_{\text{CO}}^2 P_{\text{H}_2}}{(P_{\text{H}_2\text{O}} + b' P_{\text{CO}} P_{\text{H}_2})} \quad (2)$$

where a = 2.39 x 10⁸ e^(-19700/RT) micromoles H₂+CO converted/g unreacted catalyst-min-kPa, b' = 9.50 x 10⁶ e^(-24000/RT) kPa⁻¹, T is temperature (°K), and R = 1.987 cal/°K. At low conversions (i.e. b' P_{CO} P_{H₂} >> P_{H₂O}), Eq. (2) reduces to the simplified first-order form proposed by Anderson (1956):

$$-R_{\text{H}_2+\text{CO}} = a P_{\text{H}_2} \quad (3)$$

Water, formed as a primary product of the Fischer-Tropsch reaction (Eq. 1), reacts with carbon monoxide by the water-gas-shift reaction:



This reaction proceeds essentially to equilibrium on an alkaliized iron catalyst in which case the product composition corresponds to that predicted by:

$$K_{\text{eq}} = \frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}}} \quad (5)$$

The equilibrium constant, K_{eq} , as a function of temperature T (in °K) is given by (Rossini et al.):

$$K_{\text{eq}} = 0.0102 e^{(4730/T)} \quad (6)$$

The equilibrium is far to the right at the temperatures of interest in Fischer-Tropsch synthesis.

Based on the reaction stoichiometry of Eqs. (1) and (4), the partial pressures of hydrogen, carbon monoxide, and water and the (H_2/CO) usage ratio, U , can be calculated by the following procedure:

Take as a basis 1 mole of CO and F moles of H_2 entering. F is then the inlet feed ratio of H_2/CO . Assume that the water-gas-shift reaction proceeds to equilibrium. Let z be the number of " C_nH_{2m} " moles formed by Eq. (1) and y be the number of CO_2 moles formed by Eq. (4). Material balances result in the following:

$$U = \frac{(m+n)z - y}{nz + y} \quad (7)$$

$$X_{\text{CO}+\text{H}_2} = \frac{(2n+m)z}{(F+1)} \quad (8)$$

$$X_{CO} = nz + y \quad (9)$$

$$P_{H_2} = \frac{\pi(F-mz-nz+y)}{(F+1+z-mz-nz)} \quad (10)$$

$$P_{CO} = \frac{\pi(1-nz-y)}{(F+1+z-mz-nz)} \quad (11)$$

$$P_{H_2O} = \frac{\pi(nz-y)}{(F+1+z-mz-nz)} \quad (12)$$

where π is the total pressure, and X_{H_2+CO} and X_{CO} are the fractional conversions of hydrogen plus carbon monoxide or of carbon monoxide, respectively. The equilibrium relationship given by Eq. (5) becomes:

$$K_{eq} = \frac{y(F+y-mz-nz)}{(nz-y)(1-nz-y)} \quad (13)$$

For our specific product composition, $n = 3$ and $m = 3.5$, so z can be calculated from Eq. (8), given the fractional conversion of carbon monoxide plus hydrogen and the feed ratio. Substitution of z into Eq. (13) allows y to be calculated for a specified temperature.

Results and Discussion

The ratio of rates predicted by Eqs. (2) and (3) is calculated as:

$$\frac{\text{Detailed Rate (Eq. 2)}}{\text{First-order Rate (Eq. 3)}} = \frac{1}{(1 + P_{H_2O}^{1/b} P_{CO} P_{H_2})} \quad (14)$$

Fig. 1 shows the ratio calculated from Eq. (14) as a function of conversion of H_2+CO , for various combinations of pressure, temperature and inlet gas H_2/CO ratio. A set of representative data points at 263°C is also shown for three different inlet (H_2/CO) ratios and various degrees of conversion. There is close agreement between the kinetic model and experimental data over a wide range

of conditions. Over this range of conditions, the simplified first-order rate expression (Eq. 3) is applicable at synthesis gas conversions below 40 to 70%. The simplified first-order rate becomes increasingly less accurate as carbon monoxide is depleted. This is illustrated in Fig. 2 where the ratio of rates (Eq. 14) is plotted against carbon monoxide conversion as such for the same range of parameters shown in Fig. 1. Individual curves are not depicted in Fig. 2 to avoid confusion since the range of extremes is small when CO conversion is used as the variable. The lowest line of the envelope of curves corresponds to 445 kPa, 263°C and H_2/CO feed ratio of 1.8. The highest line of the envelope occurs at 790 kPa, 263°C, and H_2/CO feed ratio of 0.55.

A theoretical plot of H_2/CO usage ratio (calculated by Eq. 7) as a function of syngas conversion is shown in Fig. 3. Over the conditions of interest (232-263°C, 445-1480 kPa, and 0.55-1.8 H_2/CO feed ratio), the curves vary significantly only with H_2/CO feed ratio because the water-gas-shift reaction, which alters the usage ratio, is independent of total pressure (Eq. 13) and is weakly dependent on temperature (Eq. 6). The usage ratio is essentially constant and similar for the different H_2/CO feed ratios at low syngas conversions; however, the usage ratio increases greatly at high percent conversions as the consumption of CO approaches completion. This is emphasized by Fig. 4. No change in the usage ratio is seen in Fig. 3 and Fig. 4 for a H_2/CO feed ratio of 0.55 as carbon monoxide and hydrogen are being consumed at about the same rate (0.59 H_2/CO usage ratio). The data plotted on Fig. 3 are for the same runs reported in Figs. 1 and 2 and agree well with the curves theoretically predicted.

Effect of Product Composition

Depending upon operating conditions, the product may vary in net H/C ratio and in average molecular weight. For present purposes the latter may be characterized by a single value of α in the Flory molecular weight distribution. Figures 5 and 6 show some representative effects of these two variables on the ratio of detailed rate to first order rate and on the usage ratio. The choice of " C_3H_7 " as a representative product corresponds to $\alpha = 0.67$. Figure 5, which may be compared to Fig. 1, and Fig. 6, which may be compared to Fig. 3, show the effect of changing the net H/C ratio for a value of $\alpha = 0.67$, expressed as " C_3H_6 " and " C_3H_8 ." The effect of a change in α is shown by " C_2H_5 " ($\alpha = 0.52$) and " C_4H_9 " ($\alpha = 0.75$).

Conclusions and Summary

From our own data and analyses of previous kinetic studies it appears that the form of Eq. 2 gives the best representation presently available of the rate of Fischer-Tropsch synthesis on iron-based catalysts. We cannot expect it to apply precisely quantitatively to other types of iron-based catalysts or even to reduced fused magnetite catalysts of different composition or reduced in a different manner. However, in the absence of specific and precise data on an iron catalyst of interest, Eq. 2 provides a basis for design estimates and interpretation of experimental data. Figs. 1 and 2 show representative sets of conditions for which Eq. (2) should be used instead of the simple kinetic expression, Eq. (3). The assumption of a simple first-order rate equation and constant usage ratio is valid to high degrees of conversion if the initial (H_2/CO) ratio is quite low (e.g. 0.55).

When this ratio is high (e.g. 1.8) the rate deviates increasingly from first order at high conversions and the usage ratio likewise changes significantly.

Literature Cited

- Anderson, R.B., in Catalysis, Vol. 4 (P.H. Emmett, ed.), Rheinhold:
New York, 1956.
- Deckwer, W.-D.; Serpemen, Y.; Ralek, M.; Schmidt, B. Chem. Eng.
Sci. 1981, 36, 765.
- Deckwer, W.-D.; Serpemen, Y.; Ralek, M.; Schmidt, B. Ind. Eng.
Chem. Process Des. Dev., 1982, 21, 231.
- Huff, G.A., Jr.; Satterfield, C.N. Ind. Eng. Chem. Process Des.
Dev. 1983, submitted
- Rossini, F.D.; Pitzer, K.S.; Taylor, W.J.; Ebert, J.P.; Kilpatrick,
J.E.; Beckett, C.W.; Williams, M.G.; Werner, H.G. A.P.I.
Research Project 44.
- Satterfield, C.N.; Huff, G.A., Jr. Chem. Eng. Sci. 1980, 35, 195.
- Satterfield, C.N., Huff, G.A., Jr. Can. J. Chem. Eng. 1982, 60, 159. "

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- Figure 4 Deviation of H_2/CO Usage Ratio as a Function
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- Figure 6 Deviation from First-Order Expression as a Function
of CO Conversion for Selected Product Compositions.
263°C, 790 kPa, $(H_2/CO)_{in} = 1.8$.

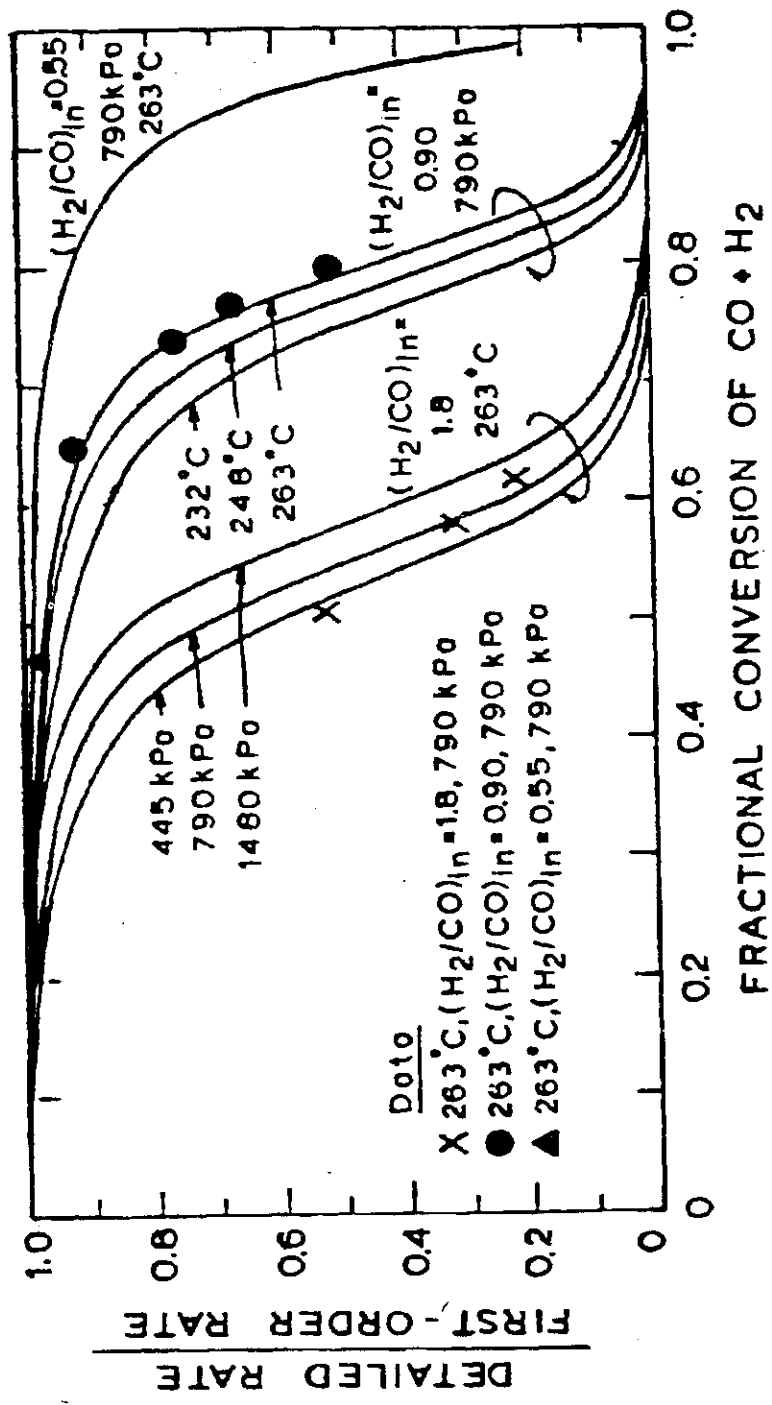


FIG. 1

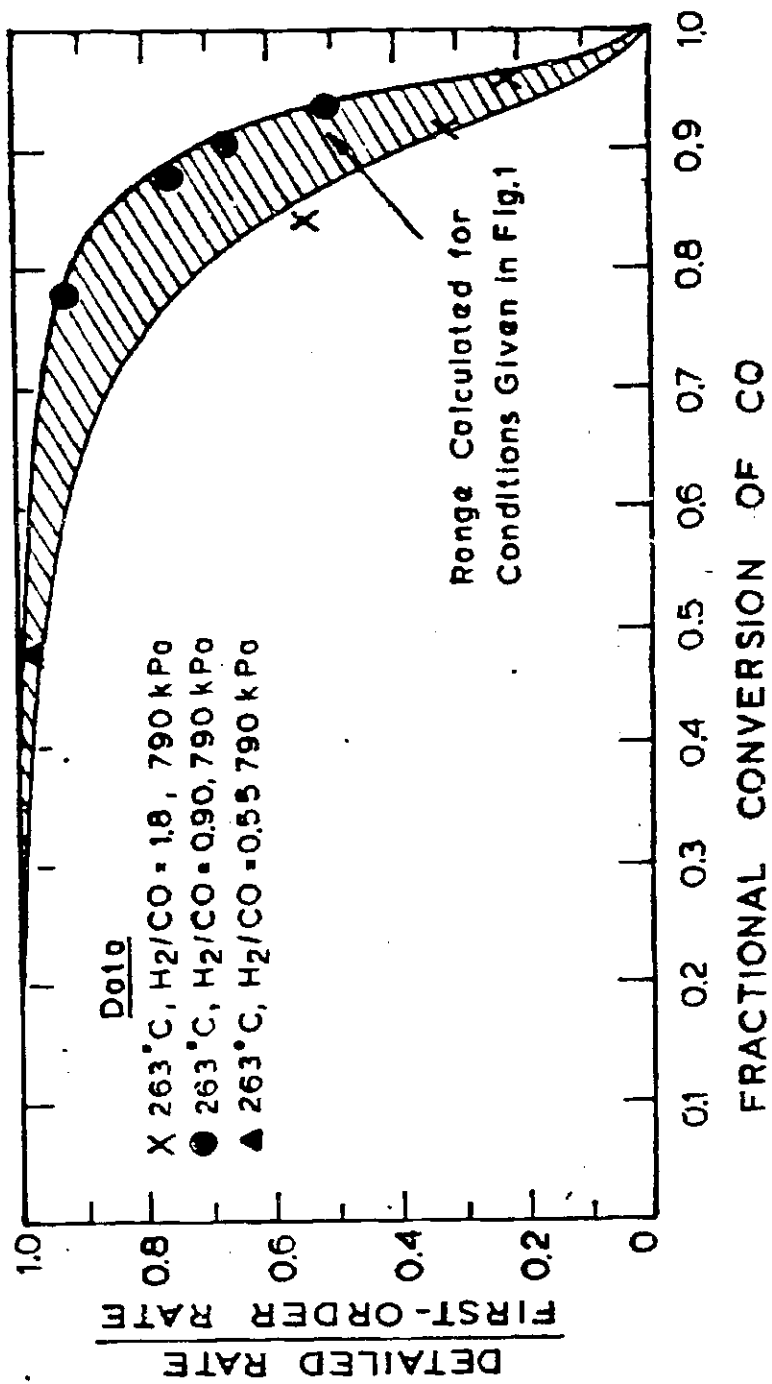


FIG. 2

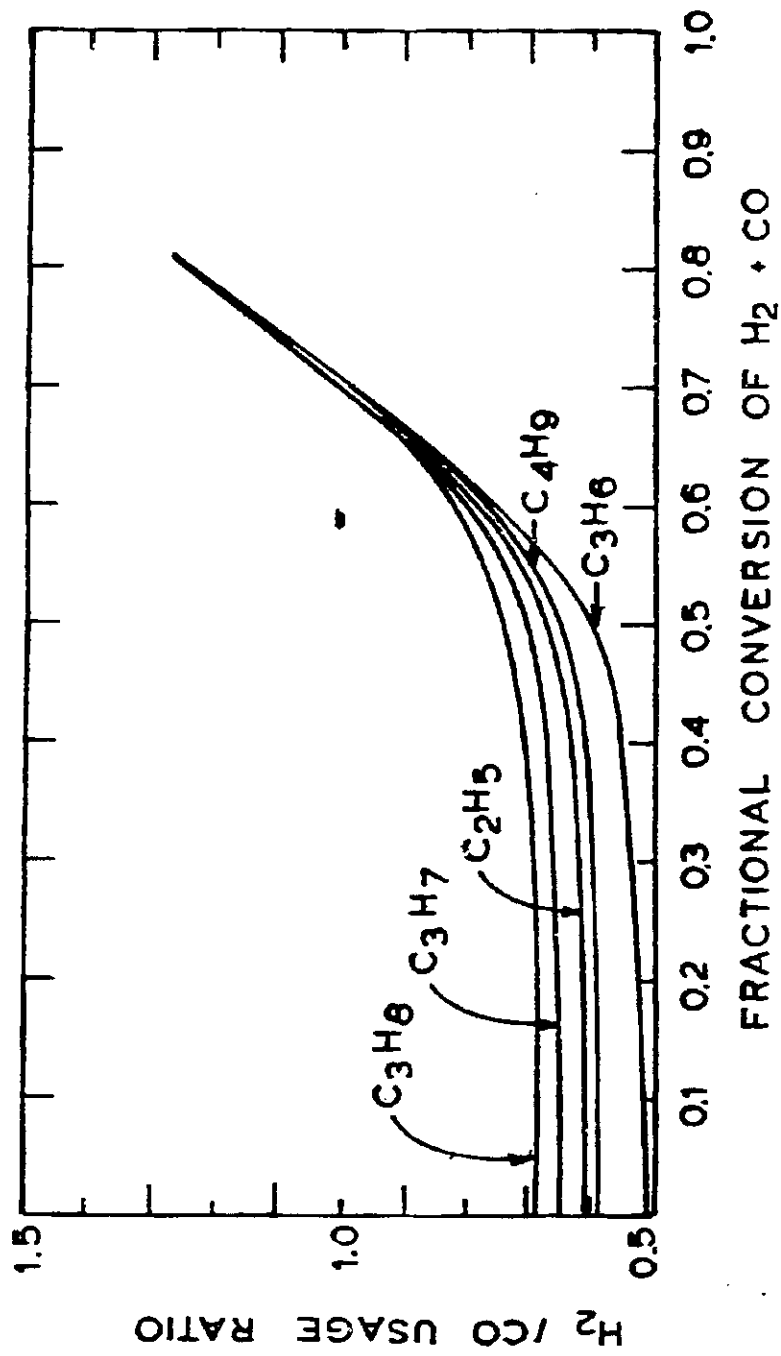


FIG. 3

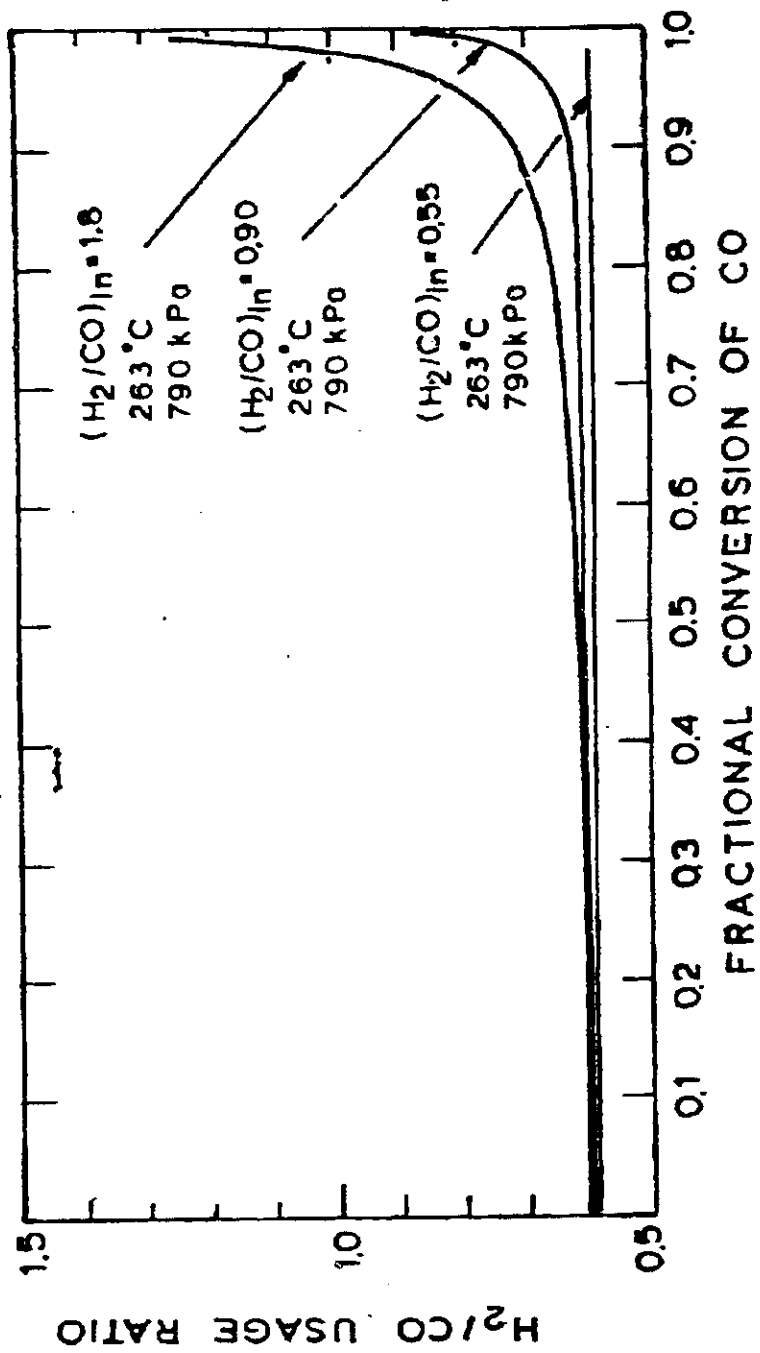


FIG. 4

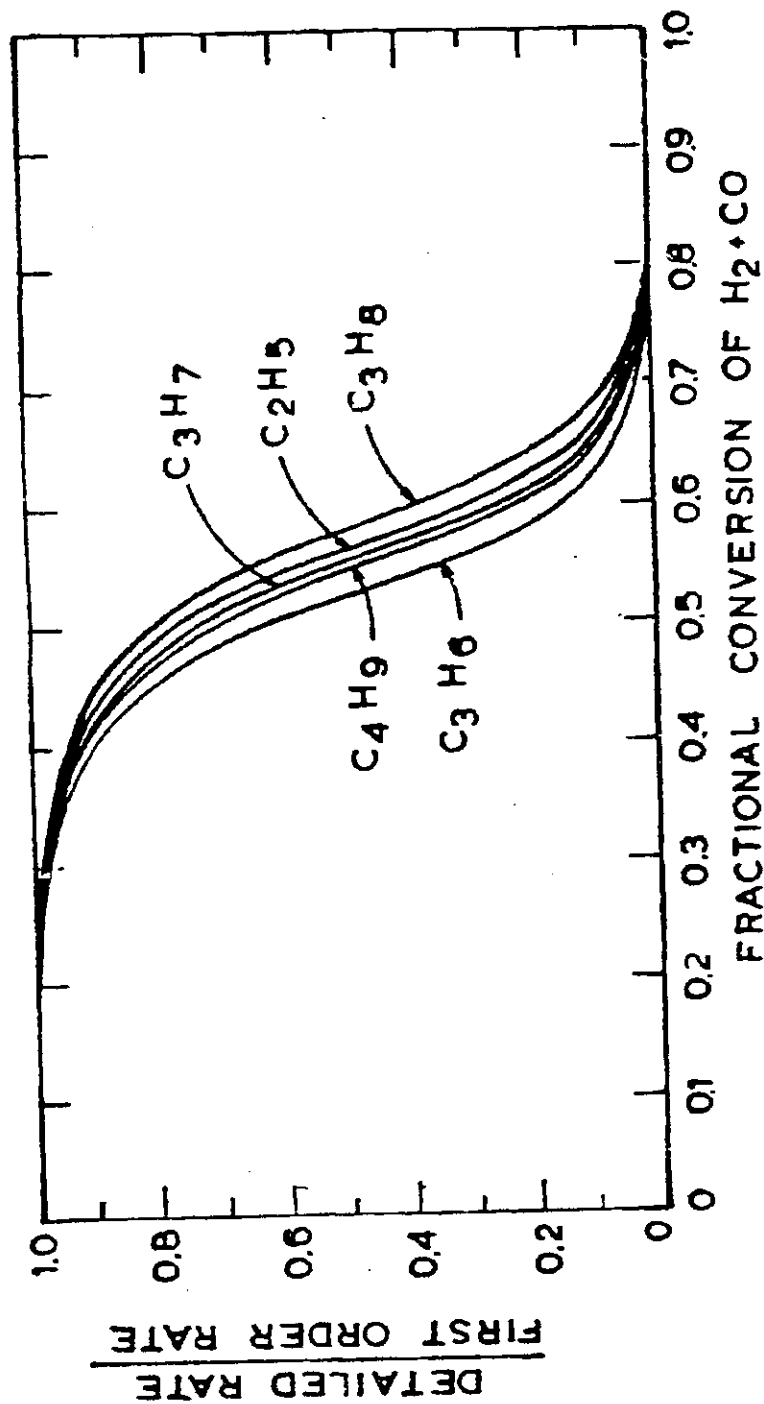


FIG. 5

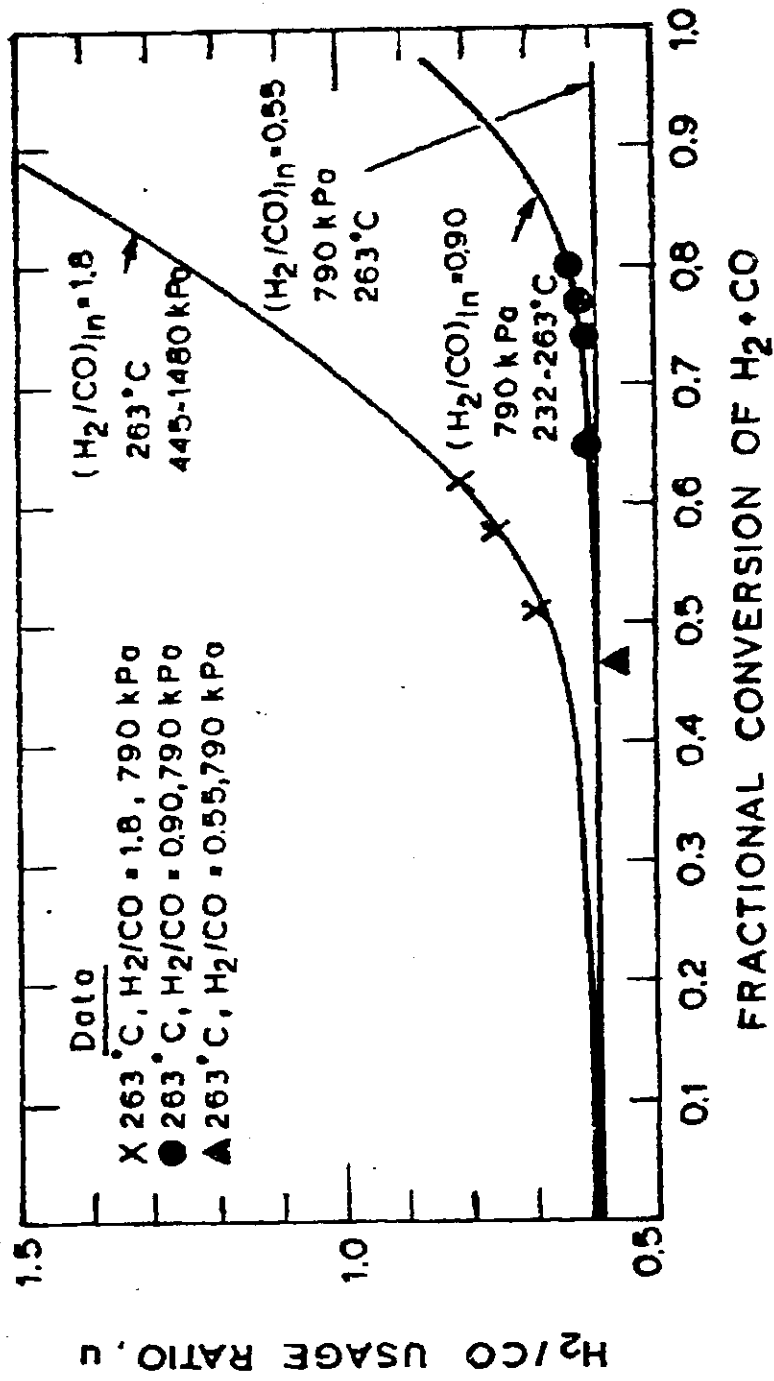


FIG. 6