TITLE: Slurry Phase Fischer-Tropsch Synthesis: Cobalt plus a Water-Gas-Shift Catalyst

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OBJECTIVE: To determine the feasibility of using a mechanical mixture of a cobalt Fischer-Torpsch catalyst and a water-gas-shift catalyst in a slurry reactor.

TECHNICAL APPROACH: The proposed mixture should make possible a combination of the product advantages of a cobalt catalyst (minimum oxygenate and carbon formation) with the operating advantages of a slurry reactor (good temperature control, flexibility in catalyst addition and removal) while feeding syngas of low H_2/CO ratio as can be produced by modern coal gasification plants.

SIGNIFICANT ACCOMPLISHMENTS: Several commercial water-gas-shift catalysts studied alone showed continuous deactivation under Fischer-Tropsch reaction conditions, but we have found that a commercial $Cu/ZnO/Al_2O_3$ catalyst, if properly reduced, shows stable activity for at least 1000 hours-on-stream. It is not detrimentally affected by high pressure, high H_2/CO ratio or the presence of alkenes. We have further demonstrated that synergism occurs between a mechanical mixture of this $Cu/ZnO/Al_2O_3$ water shift catalyst and a reduced $Co/MgO/SiO_2$ Fischer-Tropsch catalyst in a slurry reactor. Yield of $C_{10}+$ hydrocarbons is comparable to that from K-promoted catalysts of known composition but the cobalt catalyst slowly deactivated with time-on-stream.

The cobalt catalyst by itself showed essentially constant activity over 2000 hours-on-stream. Product distributions were determined at 220 and 240°C, 0.5 to 1.5 MPa, feeding syngas with H_2/CO mole ratios between 1.56 and 3.5 and over a wide range of space velocities yielding conversions of H_2 between 6 and 68% and conversions of CO between 11 and 73%. The rate of synthesis followed the expression: $-R_{H_2+CO} = a\ P_{CO}P_{H_2}/(1+bP_{CO})^2$. The weight fraction of C_{10+} increased and that of methane decreased with decreasing H_2/CO ratio in the reactor. Both selectivities were relatively insensitive to reactor pressure or temperature.

The hydrocarbon products from a cobalt catalyst, a fused iron catalyst, and a potassium- and copper-promoted, precipitated iron catalyst were compared. Although differences exist in the C_1-C_6 fraction, the C_{10}^+ fraction is somewhat similar for these catalysts.

The 1-alkene/n-alkane ratio decreased with increasing carbon number. Hydrogenation modelling revealed that a large fraction of n-alkanes which were synthesized were formed via the hydrogenation of 1-alkenes, a primary synthesis product. Increasing the reactor H_2/CO ratio decreased the 1-alkene/n-alkane ratio, while increased concentrations of CO in the reactor were seen to inhibit the isomerization of 1-alkenes to 2-alkenes.

INTRODUCTION

The work reported at this time was directed primarily to characterize the carbon number distribution of hydrocarbon products of the Fischer-Tropsch synthesis on a cobalt catalyst over a wide range of industrially-relevant conditions. Particular attention is paid to understanding the effects of process variables on the yield of desired high-molecular weight products. The reactor used in this study behaves as a CSTR and thus provides data at uniform temperature and composition which are easily interpreted.

Because incorporation or secondary reactions of alkenes may be responsible for the sensitivity of the product distributions on cobalt to operating conditions, the secondary reactions of synthesized 1-alkenes were also examined. Incorporation has been observed on cobalt in ^{14}C tracer studies by Schulz, Rao and Elstner (1970) and in alkene addition studies by Kibby et al. (1984). This may make the hydrocarbon selectivity on cobalt more sensitive to secondary reactions such as alkene hydrogenation and isomerization.

BACKGROUND

Studies of hydrocarbon distributions on cobalt catalysts date back to the early days of Fischer-Tropsch synthesis in Germany. The results from this work are well summarized by Storch et al. (1951). Data are reported for different product fractions, but not in the form of α. On the $Co/ThO_2/MgO$/kieselguhr catalysts studied, the selectivity to heavy products is seen to increase with decreasing H_2/CO ratios, go through a maximum with respect to pressure between 0.5 and 0.85 MPa and remain unaffected by conversion.

In a study of optimum ThO_2 and MgO loadings on Co catalysts, Shah and Perrotta (1976) describe hydrocarbon distributions from cobalt catalysts operated in fixed-bed reactors operated at around 200°C with a H_2/CO feed ratio of 2. A series of pressures from 0.79 to 3.04 MPa are examined. Although only limited data are provided, it can be inferred that selectivity to high-molecular weight products goes through a maximum with respect to pressure at around 0.5 MPa. Although this maximum with respect to total pressure seems somewhat anomalous, it does indicate that variations in reactant or product pressure may change the hydrocarbon distributions on cobalt catalysts.

Borghard and Bennett (1979) studied a 34% Co/SiO_2 catalyst at 2.03 MPa and 250°C with a 2 to 1 H_2/CO feed ratio and found essentially the same hydrocarbon distribution between C_{15} and C_{30} as with a precipitated Fe-Cu catalyst containing 55.4% Fe and 0.6% K. Because this type of Fe catalyst has been shown to exhibit a double-α (Donnelly and Satterfield, 1989), this would imply the existence of an α_2 around 0.9 on this cobalt catalyst. The first α can be estimated by regression of the C_3 to C_7 mole fractions from the reported gas chromatography data to be approximately 0.8. This α_1 decreases with increasing H_2/CO ratio. The products are highly paraffinic and very low in oxygenates, with 80% of the hydrocarbons being n-alkanes and up to 99% of the liquid aqueous products being water.

From experiments performed on a Co/ThO$_2$/kieselguhr and similar catalysts at 0.1 to 3.3 MPa and 175 to 210°C, H_2/CO of 1.8 to 2, Schulz (1980) makes some generalizations about product distributions. He describes two trends in the product selectivity to alkenes, one relating to hydrogenation, the other isomerization. First, the alkene to alkane ratio of products decreases with increasing carbon number, increases with increasing pressure and decreases with decreasing space velocity. Second, the ratio of 1-alkenes to total alkenes decreases with increasing carbon number, increases with increasing pressure, and decreases with increasing contact time.

Methane selectivity is reported to be in the 7 to 14 C% range and increases with increasing temperature. A double-α is reported with the break in the C_{10} region. Schulz concludes that incorporation of olefinic primary products causes the double-α on cobalt catalysts. An α_1 is calculated to be 0.82 at 180°C and 0.2 MPa for a 100 Co:9ThO$_2$:5MgO:100 kieselguhr catalyst. Although values of α_1 and α_2 are not directly reported for all sets of data, weight fractions of hydrocarbons between various carbon numbers are seen to vary dramatically with operating conditions.

In differential reactor studies performed at 250°C and atmospheric pressure, Rautavuoma and van der Baan (1981) report single chain growth probabilities as high as 0.82. The α_1 is seen to increase with increasing H_2/CO ratio which contradicts the previously-mentioned work of Storch et al (1951) and Borghard and Bennett (1979). At low conversions the concentration of 1-alkenes is so low that negligible reincorporation of alkenes into growing chains can occur. If alkene reincorporation is an important mechanism for production of high-molecular weight hydrocarbons on cobalt catalysts, then data from differential reactors may show different trends from data taken at higher conversions.

Rautavuoma and van der Baan (1981) also report that alkene to alkane ratios decrease with carbon number and increasing H_2/CO ratio. The decrease of alkene to alkane with increasing H_2/CO ratio could be explained by an increase in hydrogenation due to increased H_2 partial pressures in the reactor.

Beuther et al. (1983a and 1983b) describe Fischer-Tropsch synthesis on 100 Co: $18ThO_2$: $200Al_2O_3$ and 21.9% Co: 0.5% Ru: 2.2% ThO_2: 74.5% Al_2O_3 catalysts. Although the data from these patents are somewhat difficult to interpret, one trend in product distributions can be inferred: selectivity to higher hydrocarbons decreases with increasing temperature. This trend could be a result of increased formation of methane at higher temperatures which would contradict Schulz et al. (1982) who found that the average molecular weight of the products increased with temperature.

In a paper summarizing much of his work on cobalt Fischer-Tropsch synthesis, Schulz (1983) draws a number of conclusions about product selectivity. Three trends in alkene hydrogenation are detailed. First, alkenes are seen to hydrogenate more rapidly at low space velocities, presumably because of the greater concentration of hydrogen at low conversion. Second, hydrogenation of alkenes is seen to decrease with increasing pressure. Schulz speculates that this may be due to inhibition of the alkene adsorption by increased adsorption of CO at higher pressures. Last, the production of alkanes from alkenes is seen to increase with increasing temperature. This temperature trend can also explained in terms of competitive adsorption which would be expected to decrease at higher temperatures. With little supporting evidence, Schulz speculates that the site for hydrogenation is different from the site for primary synthesis.

In further, more detailed analysis of alkene selectivities, Schulz divides the produced alkenes into 1- and 2-alkenes. Although less conclusive trends occur than in the data with the alkenes examined as a whole, the following general trends are mentioned: formation of 2-alkenes decreases with increasing space velocity, pressure and temperature. More 2-alkenes are produced at higher carbon numbers, possibly as a result of longer residence times of higher-molecular weight 1-alkenes.

Schulz also provides information about selectivity to hydrocarbons, particularly methane. He reports that increasing temperature increases the average molecular weight of the products, but increases the selectivity to methane, which seems somewhat contradictory. At a fixed temperature, increasing pressure decreases the selectivity to methane, while the average molecular weight of the products is seen to go through a maximum. The presence of large quantities of H_2 increases the production of low molecular weight products, particularly methane. Increasing the H_2/CO ratio would, therefore, decrease α.

For catalyst with a low Co loading on Al_2O_3, Vanhove et al. (1984) gave single-α values that ranged from 0.89 (Co wt%=5) to 0.8 (Co wt%=19) in experiments at 0.1 bar and 200°C. Because the hydrocarbon distribution appears to have been changed by interactions with the acidic support, this work provides only qualitative information about potential product distributions on industrially viable catalysts.

In a study of a novel catalyst comprised of Co-Fe clusters on amine-modified silica in a fixed-bed, Roper et al. (1984) report selectivity effects at a temperature of 240°C, a H_2/CO ratio of 1 and pressures from 0.1 to 4.0 MPa. Because of the presence of the Fe and apparent catalyst deactivation during a given run, the results are difficult to interpret. At a fixed temperature and pressure, the chain growth probability, α, remains constant over a wide range of space velocities. By claiming that a constant fraction of alkenes will be readsorbed into growing chains, Roper and co-workers explain this conversion-insensitive α in terms of alkene reincorporation. This contention of alkene reincorporation was not justified by further experimentation and is somewhat speculative.

Kibby et al. (1984) performed experiments with a 30 wt% Co, 3 wt% ThO_2 on Al_2O_3 catalyst at 195°C and 0.8 MPa. Although the work was primarily focused on alkene addition, information about hydrocarbon distributions with an inlet H_2/CO ratio of 2 is given. From analysis of products up to C_{20}, α_1 and α_2 were determined to be 0.5 and 0.84, respectively. When about 10 mol% C_2H_4 was added to the feed, the value of α_1 increased to 0.8 and α_2 decreased slightly to 0.81. It appears clear that alkene reincorporation does occur, although it is hard to conclude anything directly from values for α that are so close. 25 to 35 mol% of the Fischer-Tropsch products was reported to be derived from the 10 mol% C_2H_4 that was added to the feed. A small fraction, about 2 mol%, of the product was ethanol from the added C_2H_4.

Operating in a Berty reactor at 250°C and 0.45 MPa, Sarup and Wojciechowski (1989) examined the effect of H_2/CO ratio on product distribution over a Co on SiO_2 catalyst. Products from C_1 to C_{30} were identified as predominantly linear alkanes, monomethyl isomers and some 1- and 2- alkenes. The C_3^+ products were reported to follow a single-α Schulz-Flory distribution. However, graphs of the data taken after a significant time-on-stream show a possible second α beginning in the C_{10} range. The chain growth probability is reported to decrease with increasing H_2/CO ratio. This trend is potentially due to reduced alkene reincorporation at high H_2 concentrations caused by rapid alkene hydrogenation on the cobalt catalyst. Unfortunately, Sarup and Wojciechowski do not directly report any changes in relative alkane selectivity to clarify this issue.

Fu, Rankin and Bartholomew (1986) studied 15 wt% Co on Al_2O_3 at atmospheric pressure in a differential reactor. Temperature was varied from 200°C to 235°C, inlet H_2/CO ratio from 1 to 3 and a small range of space velocities was examined. Data only at low carbon numbers were obtained. The resulting α_1 values are in the 0.5 to 0.7 range. Probability of chain growth decreased with increasing inlet H_2/CO ratio and increasing temperature.

EXPERIMENTAL

In our study, the experiments were performed in a continuous, mechanically-stirred, one-liter autoclave. The slurry reactor and ancillary equipment are described in detail elsewhere (Huff and Satterfield, 1982). The reactor and its contents are well-mixed and the reactor has been shown to operate free of heat and mass transfer limitations (Huff, 1982; Huff and Satterfield, 1982; Huff and Satterfield, 1984b).

The reactor was initially charged with 400 g of n-octacosane (>99% purity, Humphrey Chemical, Inc.). The n-octacosane had been previously recrystallized in tetrahydrofuran (>99.9% purity, Malinkrodt, Inc.) to remove a bromine impurity.

The cobalt catalyst used is a Co/MgO on SiO_2. This catalyst was prepared for us by an outside laboratory and is of the approximate composition of the cobalt catalysts used at Ruhrchemie (Storch et al., 1951). Supplied as an extrudate, the catalyst was ground and sieved to 52 to 92 μm (170 to 270 ASTM Mesh). Following sieving, 17 grams of the catalyst were placed in an external reduction vessel. The catalyst was held in this reduction unit with 7 μm stainless-steel sintered frits while hydrogen (prepurified, MedTech Gases, Inc.) was brought on-stream at a flow of 1.36 Nl/min (approximately 10,000 V/V/hr). At this flow rate, the pressure in the vessel was 0.79 MPa. The temperature of the reduction tube was increased steadily from 25°C to 330°C over 4 hours while the inlet flow rate was held constant. During this period the pressure in the reaction vessel increased to 0.97 MPa. The reduction unit was then held at 330°C for 1.5 hours. The unit was then pressured with helium and rapidly cooled The unit with the catalyst was weighed, and comparison with the initial weight indicated that the catalyst lost 18 wt.% during reduction. The reduced catalyst was added to the one-liter autoclave reactor which contained molten n-octacosane under helium.

The reactor was brought on-stream at 0.79 MPa, 187°C, and $H_2/CO=2.0$ at a flow rate of 2.0 Nl/min. The CO used in these experiments was CP grade (Granite State Oxygen, Inc.) and the H_2 was prepurified grade (MedTech Gases, Inc.). These gases pass through a 13 X molecular sieve, an activated carbon trap, and a 2 μm filter before entering the base of the reactor.

The reactor conditions were held constant for the first 65 hours and then the reactor temperature was increased to 240°C over a period of 7 hours. The reactor was then kept at 0.79 MPa, 240°C, and $H_2/CO=2.0$ at a flow rate of 2.0 Nl/min for 72 hours to allow the catalyst to achieve steady-state activity and to ensure that the overhead products were representative of those being synthesized.

Material balances at a wide range of conditions were performed over periods of 6 to 24 hours, with at least 10 hours allowed between material balances to ensure steady-state operation. When the reactor temperature or pressure was changed, at least 48 hours were allowed between material balances.

Products, liquid hydrocarbons and water, are condensed in two traps, one kept at 85°C and reactor pressure, the other at 1°C and 0.34 MPa. Material balances, including analyses of all condensed and non-condensed products, closed between 97 and 103% on oxygen, which was chosen as the material balance closure criteria because carbon and hydrogen accumulate in the reactor in the form of high molecular weight hydrocarbons (Huff, 1982; Donnelly et al., 1988). Reactor temperature was varied between 220 and 240°C. Pressures were varied from 0.5 to 1.5 MPa and H_2/CO feed ratios from 1.5 to 3.5. Total synthesis gas conversions were varied from 11 to 70% by changing space velocity between 0.085 and 0.008 Nl/min/g_{cat} (unreduced basis).

Products were analyzed with three gas chromatographs, as described by Huff et al. (1983). A Hewlett-Packard 5880 with a dimethyl silicone capillary column and flame ionization detector (FID) was used for hydrocarbon analyses of non-condensable gases and the organic phases from the hot and cold traps. Aqueous liquid samples from the hot and cold traps, and non-condensed water and oxygenated hydrocarbons were analyzed with a Hewlett-

Packard 5710 using a glass column packed with 60/80 mesh Tenax and a thermal conductivity detector (TCD). A Carle/Hach refinery gas analyzer Series S AGC 111-H was used for the analysis of non-condensable gases, particularly H_2, CO, and CO_2. Tie components, CO_2, CH_4, and C_2 and C_3 compounds, were used to match the analyses from the three gas chromatographs and provide complete product distributions for each material balance.

RESULTS AND DISCUSSION

Cobalt catalysts form mostly straight chain hydrocarbons. In the range of C_{10} to C_{20}, such products are of value as diesel and jet fuels. Heavier waxy products, in the C_{20}^+ range, can be hydrocracked back to lower molecular weight fuels. Thus, yield of high-molecular weight products is desirable.

The results presented here focus on the effects of process variables on the hydrocarbon product distributions of the synthesis. Particular attention is paid to the selectivity to the desired C_{10}^+ fraction and the undesired C_1 fraction. Because incorporation or secondary reactions of alkenes may be responsible for the sensitivity of the product distributions on cobalt to operating conditions, the secondary reactions of synthesized 1-alkenes are also examined.

Figures 1 and 2 show representative Schulz-Flory diagrams of volatile products from the cobalt catalyst. A single-α model cannot fit the C_3^+ data, which seem to be well described by a modified Schulz-Flory model, with more than one chain growth probability. The solid line in Figures 1 and 2 indicates the best-fit nonlinear regression of a double-α model as developed by Donnelly et al. (1988). Although the model of Donnelly et al. does not account for alkene incorporation and thus may be inappropriate for data from cobalt catalysts, this model was used as a basis for comparison of the data from this study with data from previous studies on iron catalysts. For the two material balances shown, α_1 is calculated to be around 0.54 and α_2 near 0.89. The "break' carbon number, the carbon number at which the contributions of both α_1 and α_2 are equal, is near 5, which is lower than is typically observed on iron catalysts. Regression of data from other material balances gave α_1 even lower than this and "break" carbon numbers as low as 2, which would correspond to a large fraction of products produced by the α_2 "site" or mechanism.

Figure 3 shows a Schulz-Flory diagram of a wax sample taken from the end-of-run slurry. The value of α_2 estimated by linear regression of the data between C_{30} and C_{53} was 0.87, which is close to that calculated by nonlinear regression above. The asymptotic linear relationship appears to hold over a wide range of carbon numbers, indicating that chain growth probability does reach a constant value at high carbon numbers.

During a material balance, analysis of data between C_1 and C_{15} provides information about the rate of synthesis of the products in this range (Huff, 1982). Because of vapor-liquid equilibrium, products at higher carbon numbers remain in the slurry liquid. Therefore, to develop a "complete" distribution of the products being synthesized, the mole fractions above C_{15} must be estimated. As discussed above, the values of α_2 calculated by nonlinear regression of volatile products were close to that calculated from the regression of non-volatile products. Thus, α_2 was regressed for each set of volatile product data and used to estimate the total mole fraction of products in the C_{15}^+ range which, for computational simplicity, was taken to be C_{16} to C_{100}. By assuming products to be all alkanes, the yield to various weight fractions of interest can be estimated. To ensure that the estimates were reasonable, only those material balances with a carbon balance, based on estimated C_1 to C_{100} products, between 95 and 105 were used. Products were divided into four weight fractions C_1, C_2-C_4, C_5-C_9, and C_{10}^+. To simplify presentation of the results, we will report only C_1 and C_{10}^+ products as representative of undesirable and desirable products, respectively.

The Effect of Operating Parameters on Hydrocarbon Selectivity

The effect of operating parameters on the weight fractions of products at C_1 and in the range C_{10}^+ are presented below.

Space Velocity

Figure 4 shows the effect of space velocity on the yield of products at 0.79 MPa, 240°C, and H_2/CO feed ratio of 2. This H_2/CO feed ratio is selected because it is near the usage ratio of cobalt and therefore, at this feed ratio, decreasing space velocity will have no effect on reactor H_2/CO. Figure 4 shows that increasing space velocity or decreasing conversion increases the fraction of C_{10}^+, while decreasing the yield of C_1 products. One possible interpretation of this is that, at higher conversions, products, such as water or alkenes, readsorb onto the surface of the catalyst and inhibit chain growth.

Pressure

Over the range of conditions studied, the pressure was seen to have very little effect on the selectivity of the synthesis to various product cuts. Figure 5 shows that, at 220°C and 0.017-0.018 Nl/min/gcat (unreduced basis) of $H_2/CO=2$ synthesis gas, the selectivity to C_1 and C_{10}^+ products remains constant over a range of total reactor pressure of 0.5 to 1.5 MPa. This tends to indicate that the trend observed in space velocity is related to the ratio of products to reactants, rather than to total product concentration.

The conclusion that pressure has no effect on the selectivity of the synthesis contradicts Storch et al. (1951) and Shah and Perrotta (1976) who found that selectivity to high-molecular weight hydrocarbons went through a maximum with respect to temperature in fixed-bed reactors. The data for these studies were collected, for the most part, at a fixed inlet H_2/CO ratio and varying space velocities. Thus, product-to-reactant ratios varied down the length of the bed, making any conclusion about the effect of pressure difficult to de-convolute from the effect of space velocity.

Temperature

Figure 6 shows the dependence of the weight fractions of C_1 and C_{10}^+ for total synthesis gas conversions in the range 31 to 33%. As indicated by the figure no real trend is observed for comparable conversions. The temperature data are presented at comparable conversion, rather than space velocity, because the ratio of product to reactant concentration appears to have a marked effect (Figure 4). Thus, in order to compare comparable product to reactant ratios, data at similar total synthesis gas conversions were used. Within the scatter at each temperature, it is reasonable to conclude that no trend exists.

The conclusion that temperature has little overall effect on the synthesis is not inconsistent th the contradictory conclusions of Schulz (1982) and (1983) that increasing temperature increases methane yield and increases the average molecular weight. The data of Schulz are taken over a lower temperature range from 175 to 210°C, which may account for the differences in his conclusions. Further, Schulz may not have compared data at similar conversions, which could be important as discussed above.

Reactor H_2/CO Ratio

Figure 7a shows the effect of reactor H_2/CO ratio on the relative yield of products at C_1 at 230°C. Increasing reactor H_2/CO ratios increases the relative weight fraction of C_1 at all temperatures, although the trend more apparent at lower temperatures (data not shown). Methane may be formed by a mechanism separate from chain growth, which may have a positive dependence on the P_{H_2}/P_{CO} ratio.

The effect of reactor H_2/CO ratio on the fractional yield of products in the C_{10}^+ range at 220, 230, and 240°C was also studied. Increasing reactor H_2/CO ratio decreases the yield of high-molecular weight products relative to total hydrocarbons synthesized. This decrease in yield of C_{10}^{+} products can be primarily attributed to the increase in rate of production of lighter-molecular weight products, particularly methane.

Storch et al. (1951), Borghard and Bennett (1979), Schulz (1983), and Fu et al. (1986) all conclude that increasing the ratio of H_2/CO increases the yield of undesired lower-molecular weight products, C_1, at the expense of desired high-molecular weight products, C_{10}^{+}. Only Rautavouma and van der Baan (1981), who operated differentially at atmospheric pressure, conclude that increasing H_2/CO increases production of high-molecular weight hydrocarbons. At low conversions and pressures the concentration of synthesized 1-alkenes may be so low that negligible reincorporation of alkenes into growing chains can occur. If alkene reincorporation is an important mechanism for production of high-molecular weight hydrocarbons on cobalt catalysts as is suggested by the incorporation studies of Schulz et al. (1970), then data from differential reactors may show different trends from data taken at higher conversions.

Selectivity of the Synthesis to Various Product Classes

Figure 9 and 10 show Schulz-Flory diagrams including the distribution of three major product classes, n-alkanes, 1-alkenes, and n-alcohols. Three other components were observed in much lower concentrations than these at each carbon number; in order of relative abundance in products, they are 2-alkenes, branched alkanes, and aldehydes (only at C_2 and C_3 in very low concentrations). Methane lies above the line that would be predicted by a double-α Schulz-Flory mechanism, while C_2 products lie below, as is characteristic of most Schulz-Flory diagrams of hydrocarbon products from the Fischer-Tropsch synthesis. The reasons for this are detailed elsewhere (Donnelly et al. (1988)).

Both the n-alkanes and n-alcohols exhibit a double-α type distribution; that is, at low carbon numbers, the mole fraction of products drops off quickly, while, at higher carbon numbers, the mole fraction drops off more slowly. The 1-alkenes appear to follow a single-α type distribution. The extent to which observed products represent the primary synthesis versus secondary reactions varies depending on reactor conditions. The 1-alkene, which is presumed to be the primary product of the synthesis Schulz (1983), may subsequently be hydrogenated to an n-alkane or isomerized to a 2-alkene. The ratio of 1-alkene/n-alkane and 1-alkene/2-alkene both decrease with increasing carbon number as was also observed by Schulz (1980) and Rautavuoma and van der Baan (1981). As will be shown later, a large fraction of n-alkanes appear to be produced by the hydrogenation of 1-alkenes. Therefore, conclusions made about this type of a component Schulz-Flory diagram, assuming independent mechanisms for the production of 1-alkenes and alkanes, may be misleading.

Secondary Reactions of 1-Alkenes

In order to understand the effects of operating conditions on the secondary reactions, the rate of synthesis of ethane, n-butane, and 2-butene were studied. Ethane is examined because it represents hydrogenation only; the behavior of the C_4 compounds is presented as representative of that of the C_3^+ products. As discussed by Hanlon (1985), Hanlon and Satterfield (1988), and Donnelly and Satterfield (1989), C_4 products are the highest molecular weight products which exist only in the vapor phase at room temperature which eliminates splitting of products between vapor and liquid phases in the traps.

These analyses of the secondary reactions of the 1-alkenes may only yield general trends, indicative of the secondary of 1-alkenes on the cobalt catalyst. To understand fully the behavior of 1-alkenes, it may be necessary to add 1-alkenes to the synthesis gas feed. Alkene additions are planned in future runs with this catalyst.

Rate of Ethane Formation from Ethene

Figures 11a and 11b show the dependence of the rate of formation of ethane on the ratio of $P_{C_2H_4}P_{H_2}/P_{CO}$ in the reactor at 220 and 240°C respectively. This assumes that the rate of ethane formation is a simple hydrogenation process which is inhibited by adsorbed CO. While there is considerable scatter in the data, both figures indicate that a considerable amount of the variance in the rate of ethane formation can be explained by such a simple model. The vertical axis intercept of these figures represents the amount of ethane that is produced as primary product. While this intercept is non-zero, over most of the range of operating variables studied, the amount of ethane produced by primary synthesis is less than half of the total amount synthesized.

Rate of n-Butane Formation from 1-Butene

Figures 12a and 12b show the dependence of the rate of formation of n-butane on the ratio of $P_{C_4H_8}P_{H_2}/P_{CO}$ in the reactor at 220 and 240°C respectively. Again, a simple hydrogenation process which is inhibited by adsorbed CO is assumed. While there is considerable scatter in the data, particularly at 240°C, both figures indicate that the rate of n-butane formation increases with increasing $P_{C_4H_8}P_{H_2}/P_{CO}$. The vertical axis intercept of these figures is related to the amount of n-butane produced in the primary synthesis. Over the range of operating variables studied, the amount of n-butane produced by primary synthesis is generally less than half of the total amount synthesized.

The behavior of these two simple hydrogenation models is consistent with the observations of Schulz (1980) and (1983) and Rautavuoma and van der Baan (1981) that increasing hydrogen to carbon monoxide ratio decreases the 1-alkene/n-alkane ratio.

Rate of 2-Butene Formation from 1-Butene

2-alkenes are generally not considered to be a product of the primary synthesis, but are assumed to be produced solely by isomerization of 1-alkenes (Schulz, 1983). Thus a model was developed which accounted for all of the production of 2-butene in terms of 1-butene. A simple Langmuir-Hinshelwood type relationship of the following form is proposed:

$$R_{2\text{-butene}} = kP_{1\text{-butene}}/(1+K_{CO}P_{CO}) \qquad (1)$$

This assumes that the rate of 2-butene formation is simply proportional to the concentration of 1-butene and inhibited by carbon monoxide. Eq 1 can be linearized as follows:

$$P_{1\text{-butene}}/R_{2\text{-butene}} = 1/k + K_{CO}/k\ P_{CO} \qquad (2)$$

Figures 13a and 13b depicts the dependence of the rate of formation of $P_{1\text{-butene}}/R_{2\text{-butene}}$ on P_{CO} at 220 and 240°C respectively. Both figures show that increasing P_{CO} will decrease the rate of 1-butene isomerization.

The conclusion made by Schulz (1983) that the ratio of 1-alkenes/total alkenes increases with increasing total pressure could be explained over tne narrow range of H_2/CO studied (1.8 to 2) by a relationship such as eq 1.

Summary of Secondary Reaction Studies

As discussed above, these analyses represent only a preliminary examination of the secondary reactions of the 1-alkenes on cobalt catalysts. However, three interesting conclusions can be drawn from this study.

First, a large fraction of synthesized alkanes and all 2-alkenes appear to be produced by secondary reactions. As discussed earlier, this makes interpretation of component Schulz-Flory diagrams difficult.

Second, increasing the reactor H_2/CO ratio increases the ratio of alkane to 1-alkene at each carbon number. If synthesized 1-alkenes re-adsorb onto the catalyst surface and incorporate into growing chains, then the decrease in 1-alkene concentration (relative to n-alkane concentration) at increased

P_{H_2}/P_{CO} may explain the decrease in high-molecular weight products at high P_{H_2}/P_{CO}.

Finally, increasing the concentration of carbon monoxide may decrease the amount of 2-alkene formation. If 1-alkene incorporation plays a role in hydrocarbon production, then again the decrease in 1-alkene concentration (relative to 2-alkene concentration) at low values of P_{CO} may explain the decrease in high-molecular weight products at high P_{H_2}/P_{CO}.

COMPARISON OF CARBON NUMBER DISTRIBUTION WITH IRON-BASED CATALYSTS

Figure 14 shows Schulz-Flory diagrams from three catalysts studied in this laboratory. The cobalt catalyst is from the data presented here at 240°C, 0.51 MPa, and 0.029 Nl/min/gcat of H_2/CO=1.86 synthesis gas (material balance [illegible]). The potassium- and copper-promoted, precipitated iron catalyst is the so-called Ruhrchemie catalyst studied in detail by Donnelly and Satterfield (1989). The data shown here were taken at 263°C, 2.57 MPa, and 0.034 Nl/min/gcat of H_2/CO=0.73 synthesis gas (material balance RC3.16) (Donnelly, 1989). The fused magnetite catalyst is the triply-promoted ammonia synthesis catalyst designated C-73 by United Catalysts. The data shown here were from a material balance at 263°C, 0.51 MPa, and 0.015 Nl/min/gcat of H_2/CO=0.55 synthesis gas (material balance FE3.46 (Huff, 1982).

Figure 14 indicates that the three catalysts synthesize comparable amounts of the desired high-molecular weight hydrocarbons. The cobalt catalyst synthesizes a far larger amount of C_1 product and far less of C_2 to C_5 products. Nonlinear regression of the data yields an α_1 of 0.66, α_2 of 0.91, and a "break" carbon number, Ω, of 7.5 for the Ruhrchemie catalyst (Donnelly, 1989), α_1 of 0.59, α_2 of 0.9, and Ω=7 for the fused magnetite (Donnelly et al., 1988), and α_1 of 0.4, α_2 of 0.88, and Ω=2 for the cobalt catalyst. While the double-α formulation may not be appropriate for cobalt catalysts it does provide a benchmark for understanding why the catalysts exhibit such differing behavior at low molecular weights yet similar behavior at high molecular weights. The cobalt catalyst appears to have a much lower first chain growth probability, as evidenced by the sharp drop off in C_3 to C_5, but the α_1 contributes far less to the total product distribution, as indicated by the extremely low value of Ω. See also Table 1.

KINETICS

A detailed study of the kinetics was also made and is presented elsewhere. The best kinetic expression is given on Table 2 and compared to two for iron.

CONCLUSIONS

The effects of selected process variables on the hydrocarbon product distribution have been determined. Increasing space velocity or decreasing reactor H_2/CO ratio is seen to decrease the relative yield of undesired C_1 while increasing the yield of desired C_{10}^+ products. Reactor temperature and pressure have little effect on the product distribution.

The selectivity the catalyst to 1-alkanes, n-alkanes, and 2-alkenes is shown to depend on reactor H_2/CO ratio and on total CO concentration. These 1-alkene and weight fraction yield data are consistent with a model which would account for the re-adsorption of 1-alkenes into growing chains on the catalyst surface. A study of the reactions of selected 1-alkenes added to the synthesis gas feed could provide information on the propensity for 1-alkenes to incorporate.

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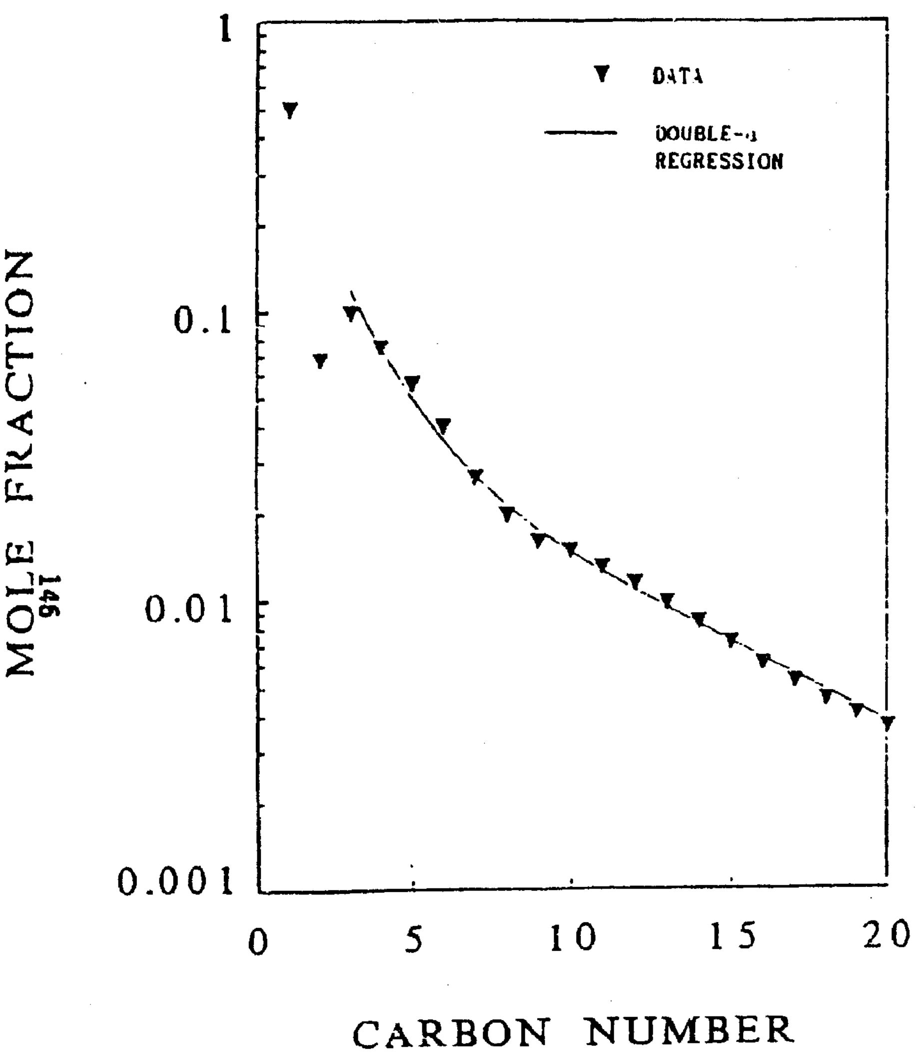

FIGURE 1. Schulz-Flory diagram of volatile products at 230°C, 0.79 MPa, and 0.020 Nl/min/gcat (unreduced basis). $H_2/CO=1.5$. $\alpha_1=0.54$, $\alpha_2=0.88$, and $\Omega=5$

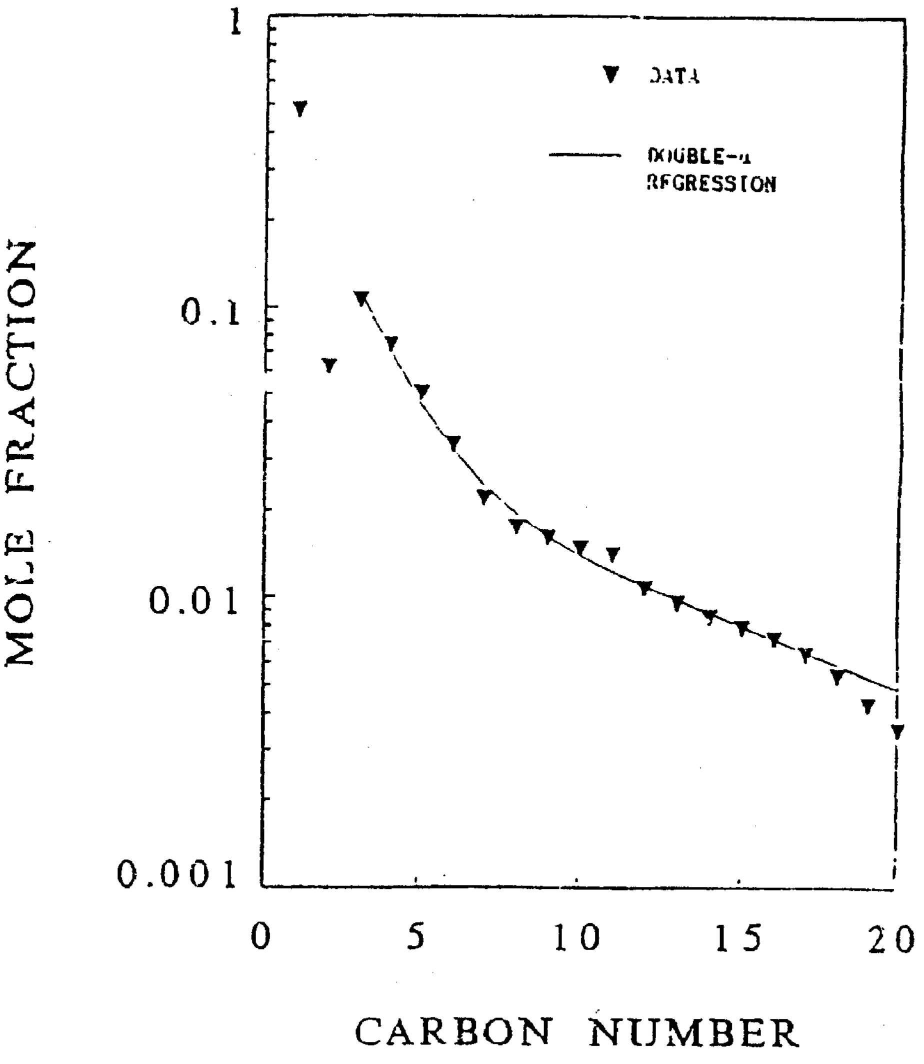

FIGURE 2. Schulz-Flory Diagram of volatile products at 220°C, 1.48 MPa, and 0.032 Nl/min/gcat (unreduced basis). $H_2/CO=1.6$. $\alpha_1=0.54$, $\alpha_2=0.91$, and $\Omega=5.4$.

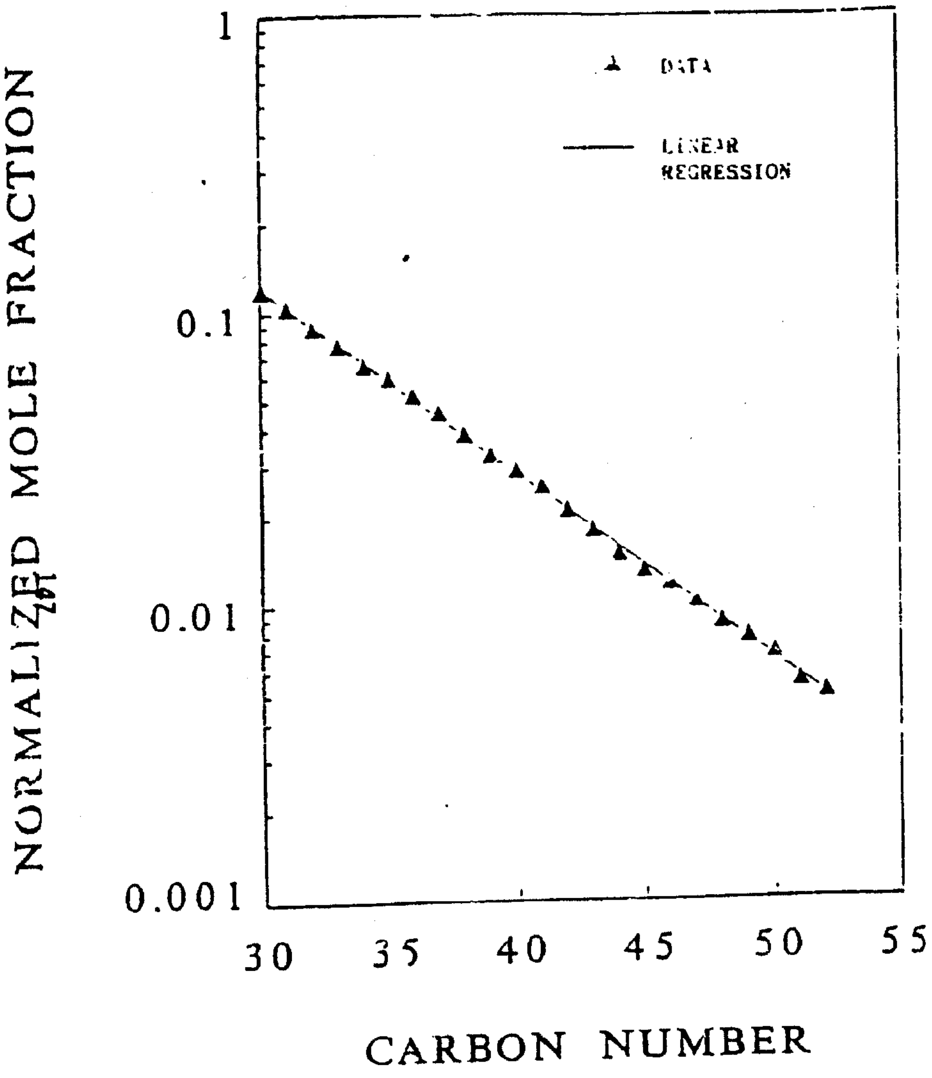

FIGURE 3. Schulz-Flory Diagram of end-of-run slurry. Linear regression of C_{30} to C_{53} products, shown as the solid line, gives α_2=0.87.

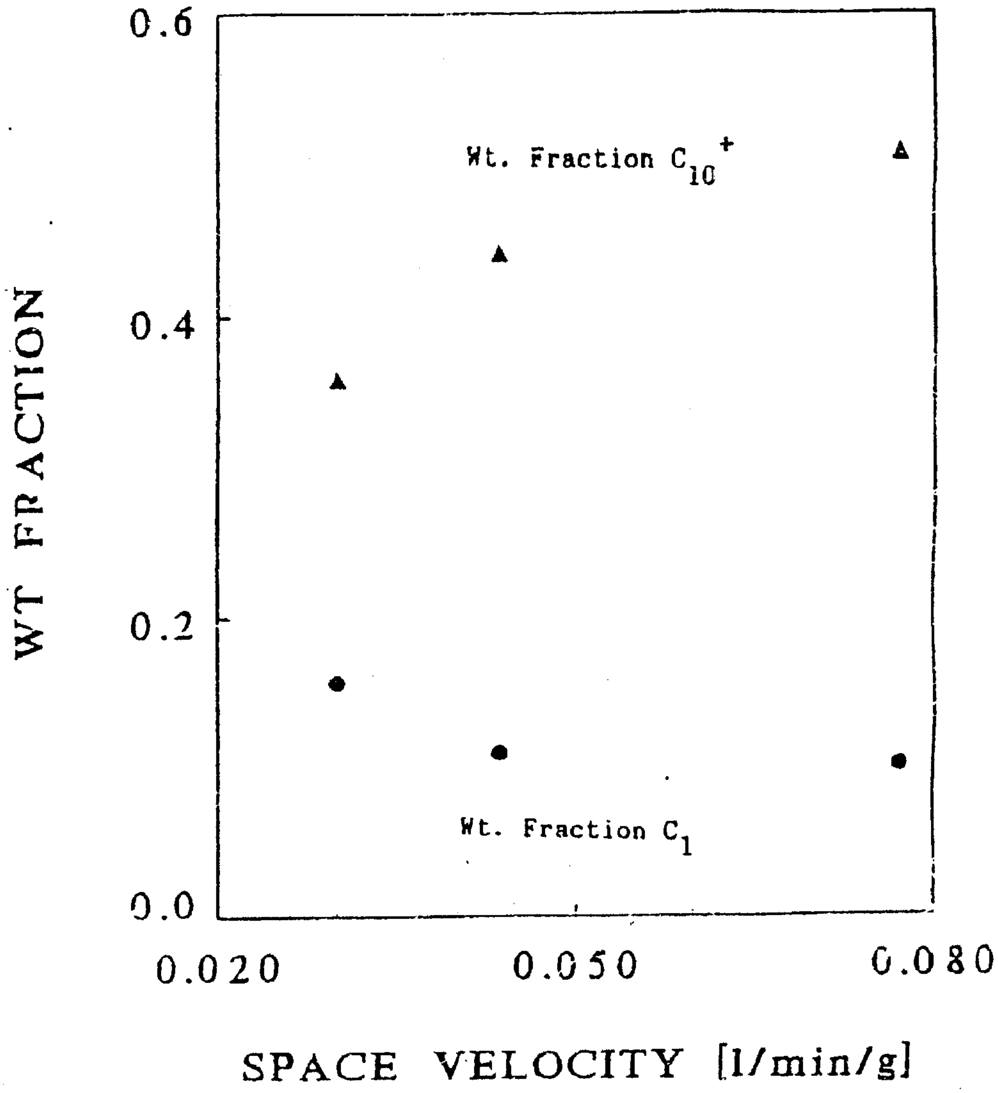

FIGURE 4. Dependence of product weight fractions on space velocity at 0.79 MPa, 240°C, and H_2/CO=2.

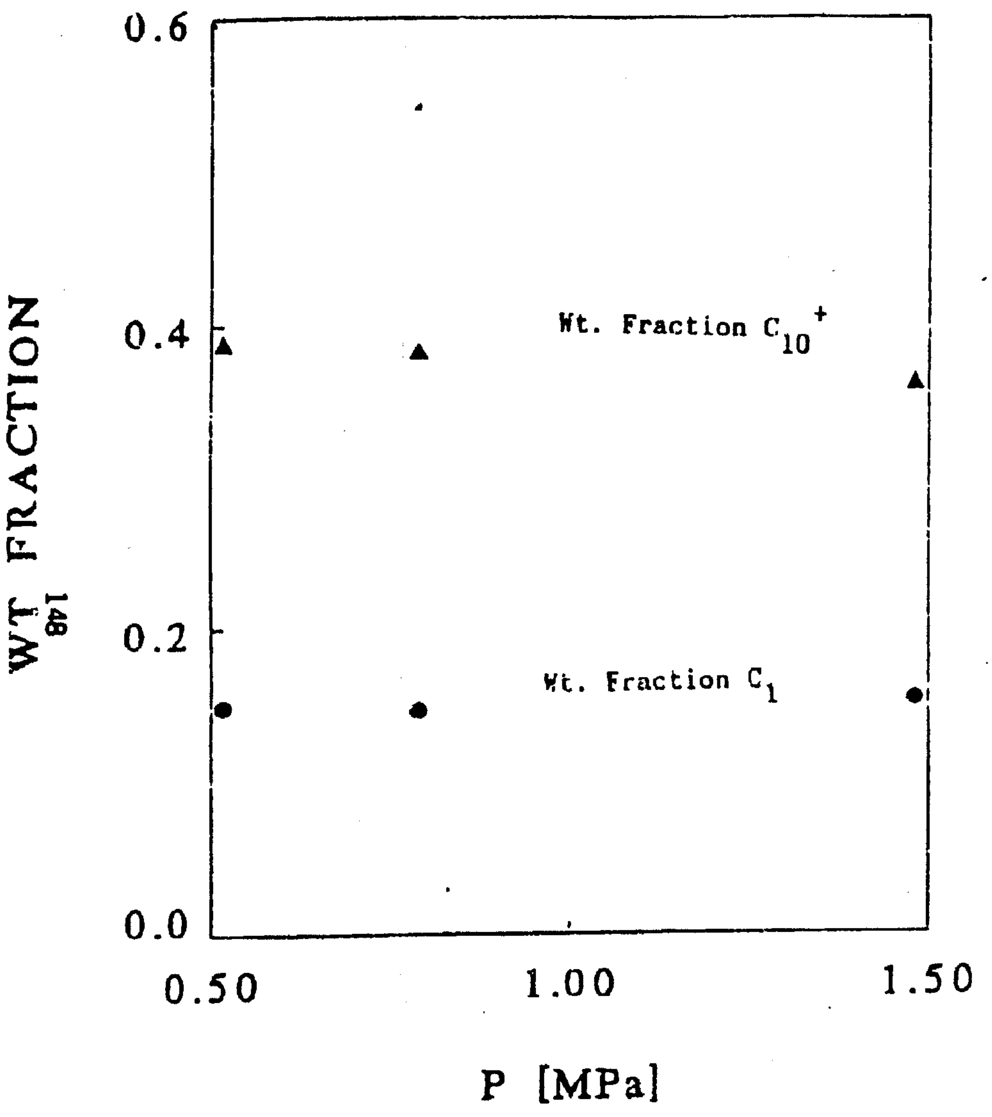

FIGURE 5. Dependence of product weight fractions on reactor pressure at 240°C, 0.017 to 0.018 Nl/min/gcat (unreduced basis), and $H_2/CO=2.1$.

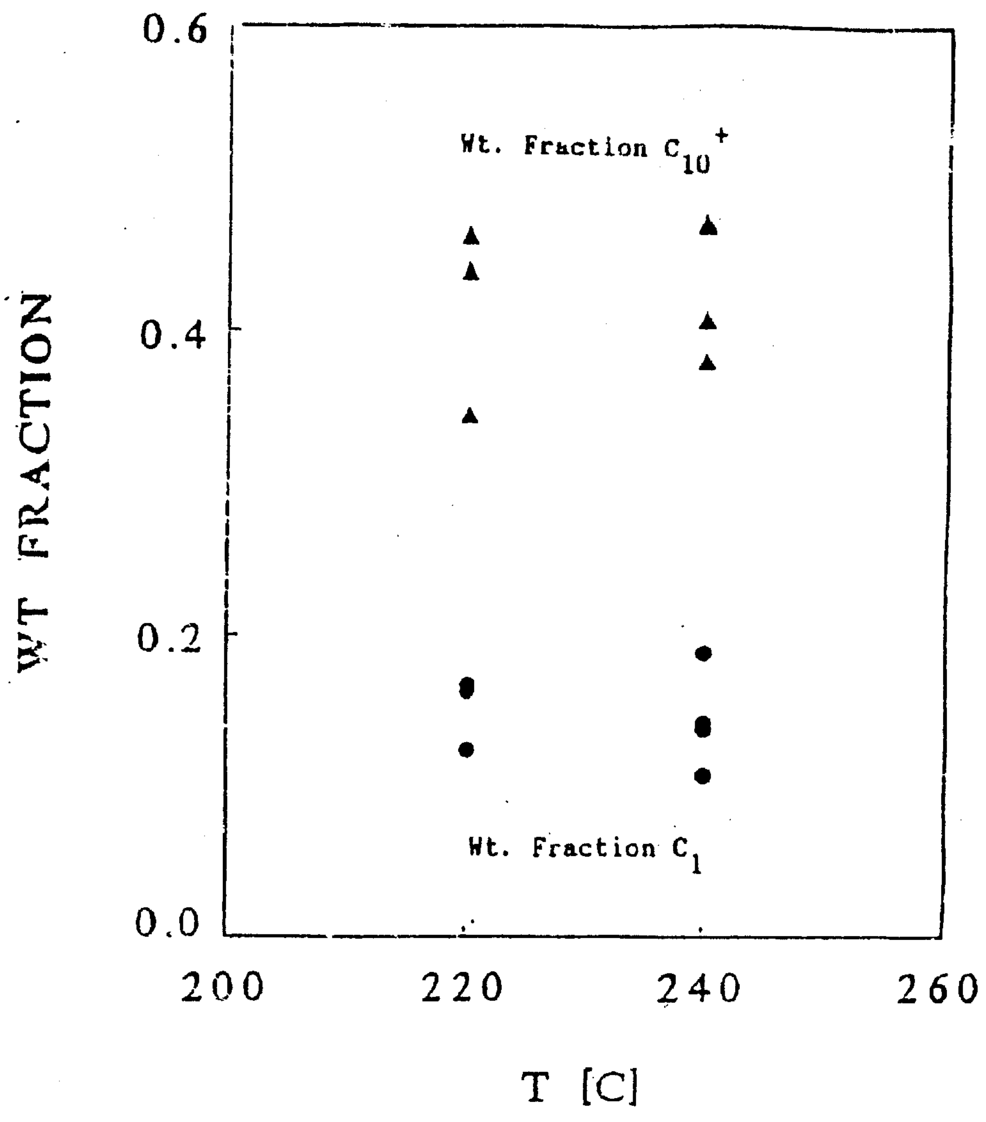

FIGURE 6. Dependence of product weight fractions on reactor temperature at conversions of total synthesis gas in the range of 31 to 33 mol%.

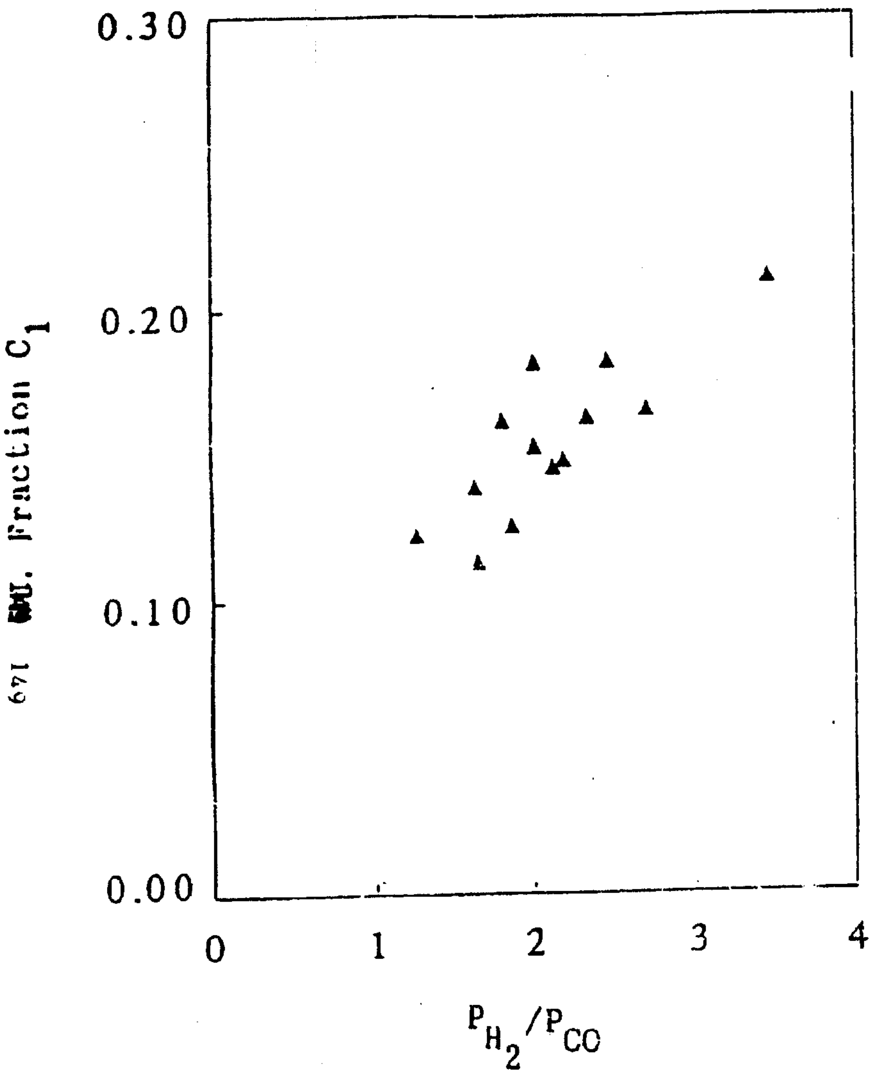

FIGURE ia Dependence of fractional yield of C_1 products on reactor H_2/CO ratio at 220°C.

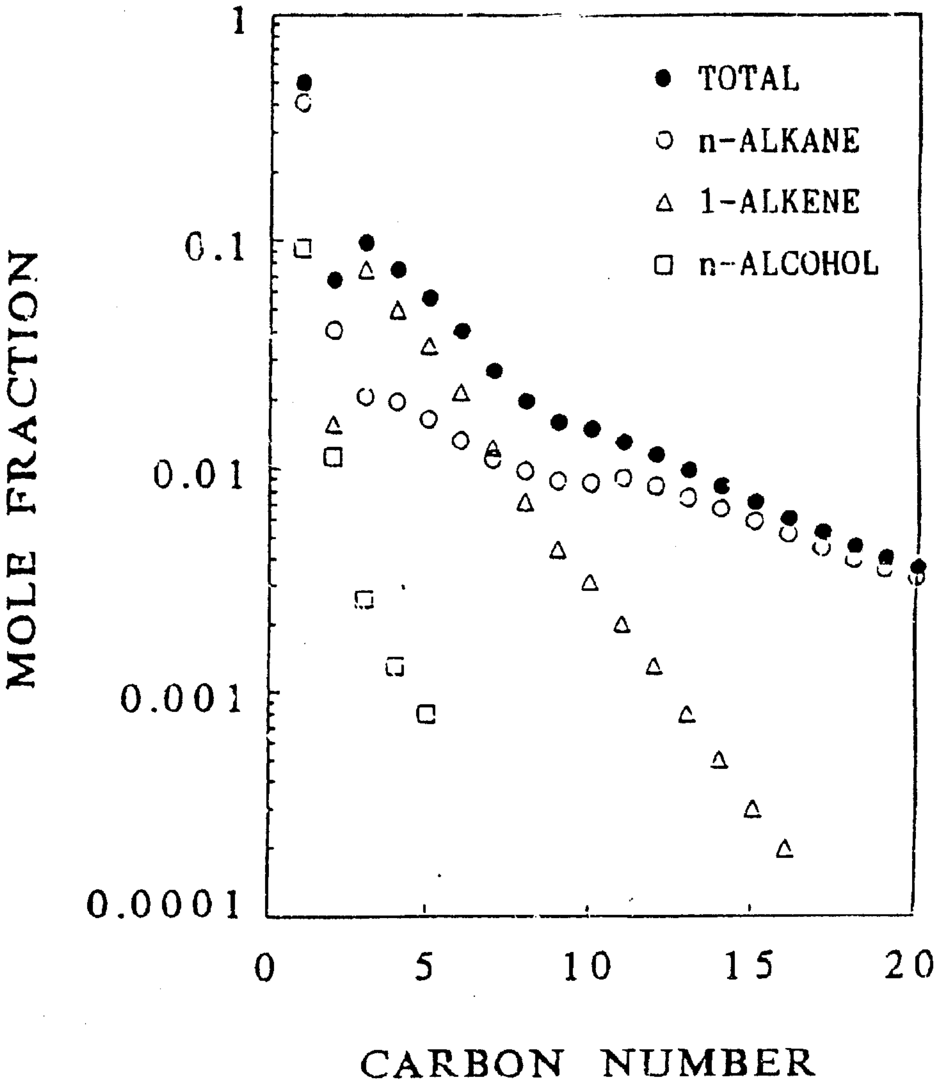

FIGURE 9. Schulz-Flory diagram of volatile products at 230°C, 0.79 MPa, and 0.020 Nl/min/gcat (unreduced basis), H_2/CO=1.5.

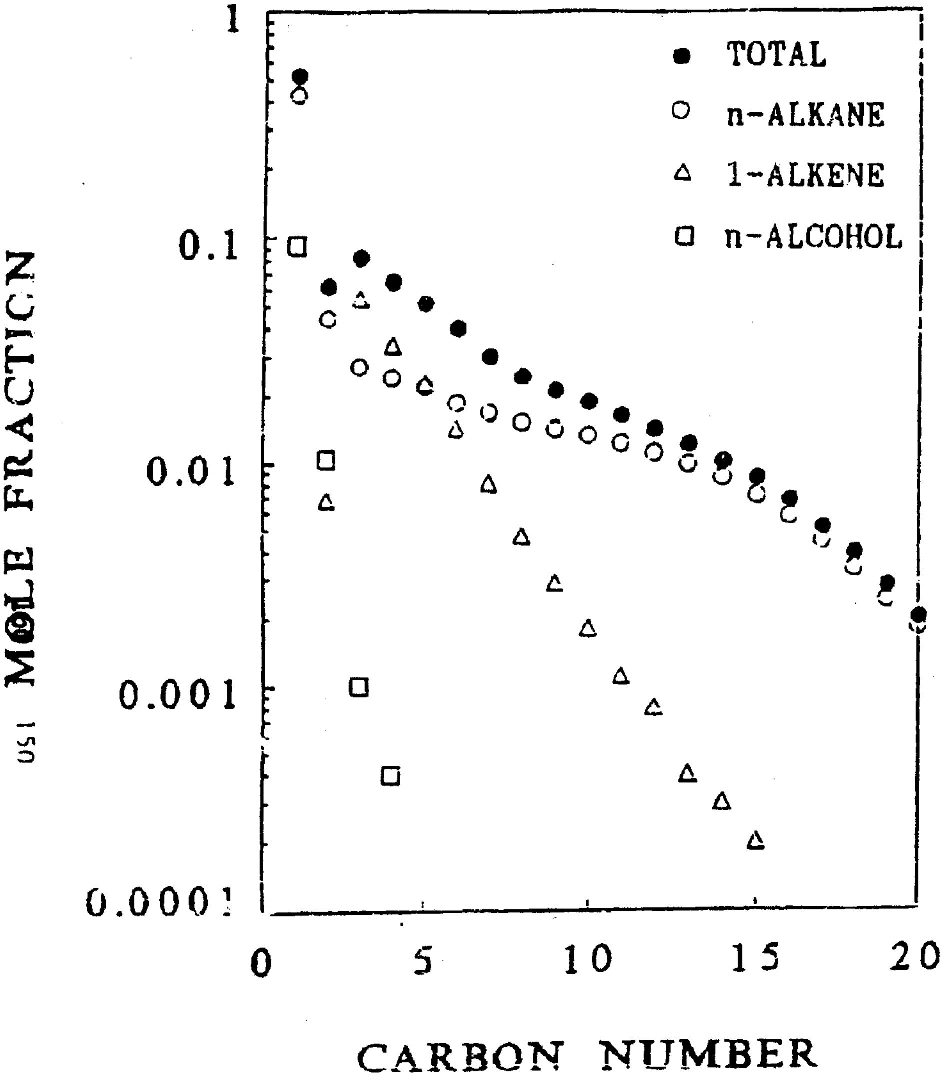

FIGURE 10. Schulz-Flory diagram of volatile products at 240°C, 0.79 MPa, and 0.035 Nl/min/gcat (unreduced basis). $H_2/CO=2.2$.

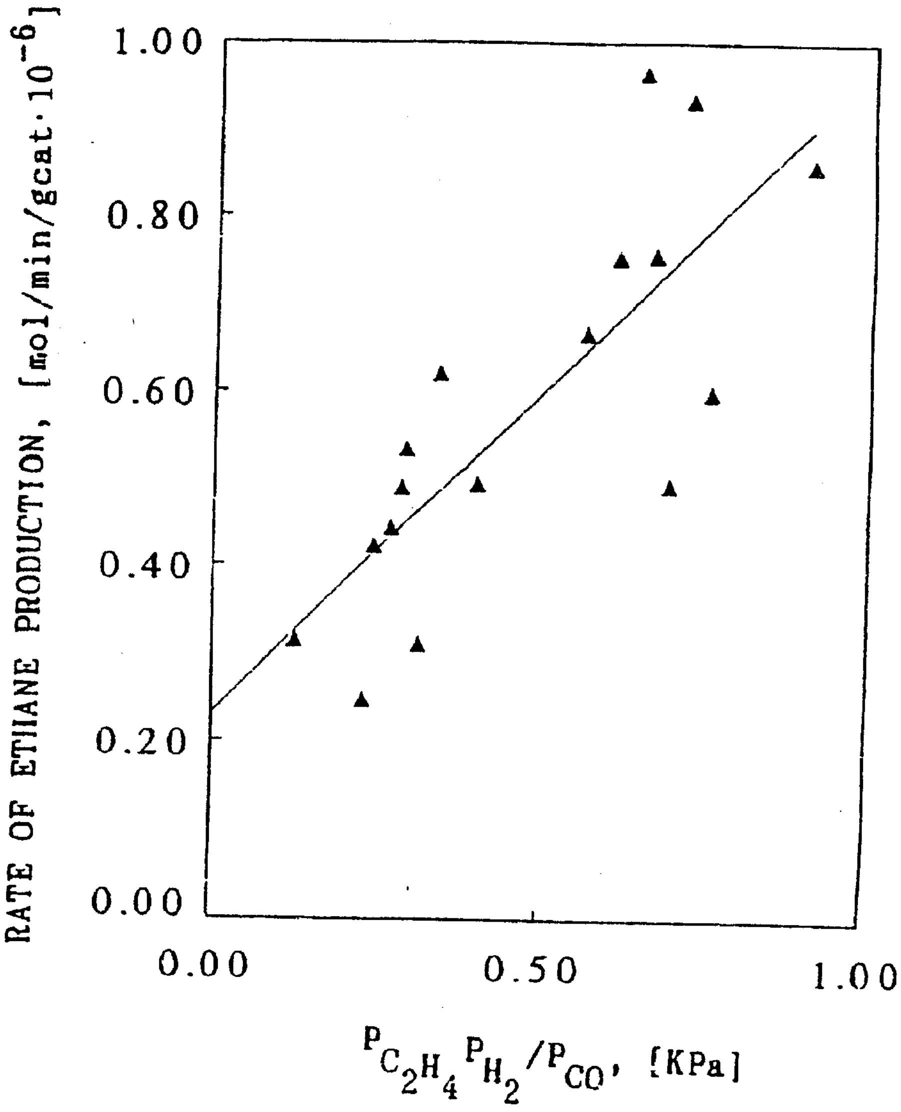

FIGURE 11a. Rate of ethane production following a simple hydrogenation model at 220°C.

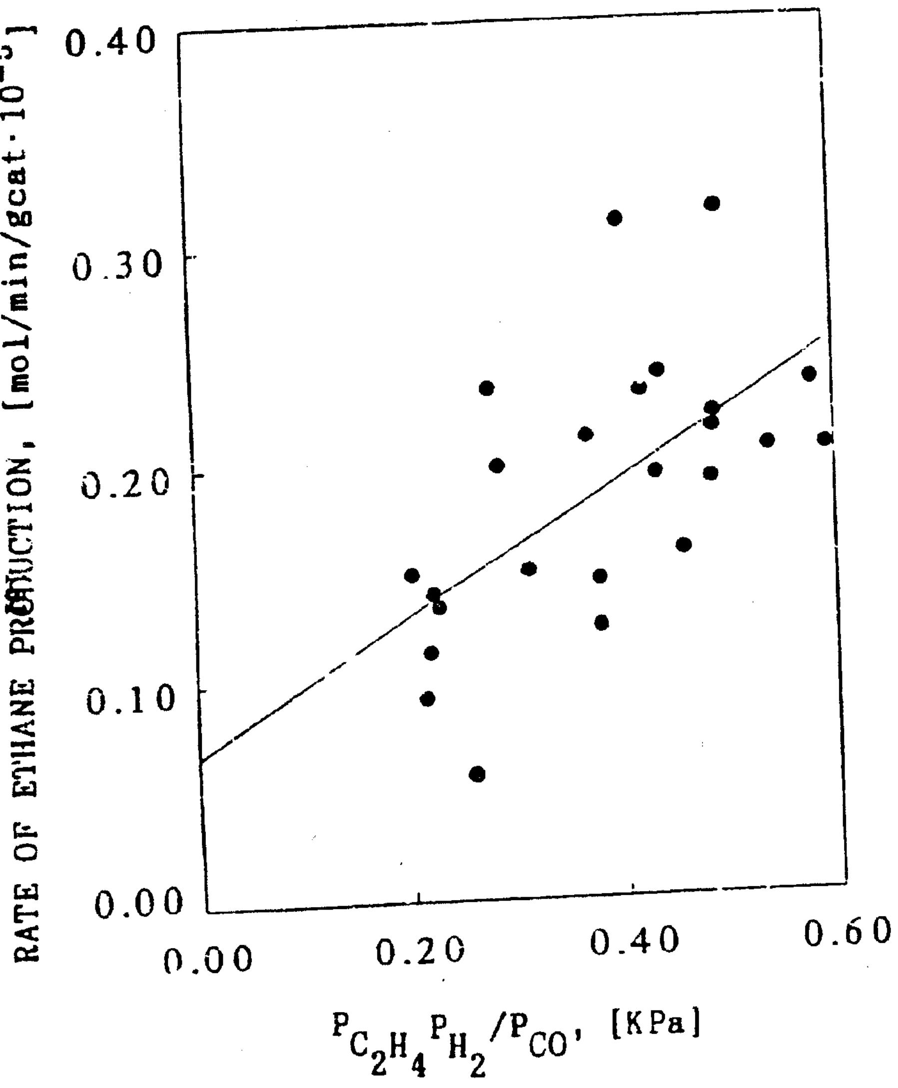

FIGURE 11b. Rate of ethane production following a simple hydrogenation model at 240°C.

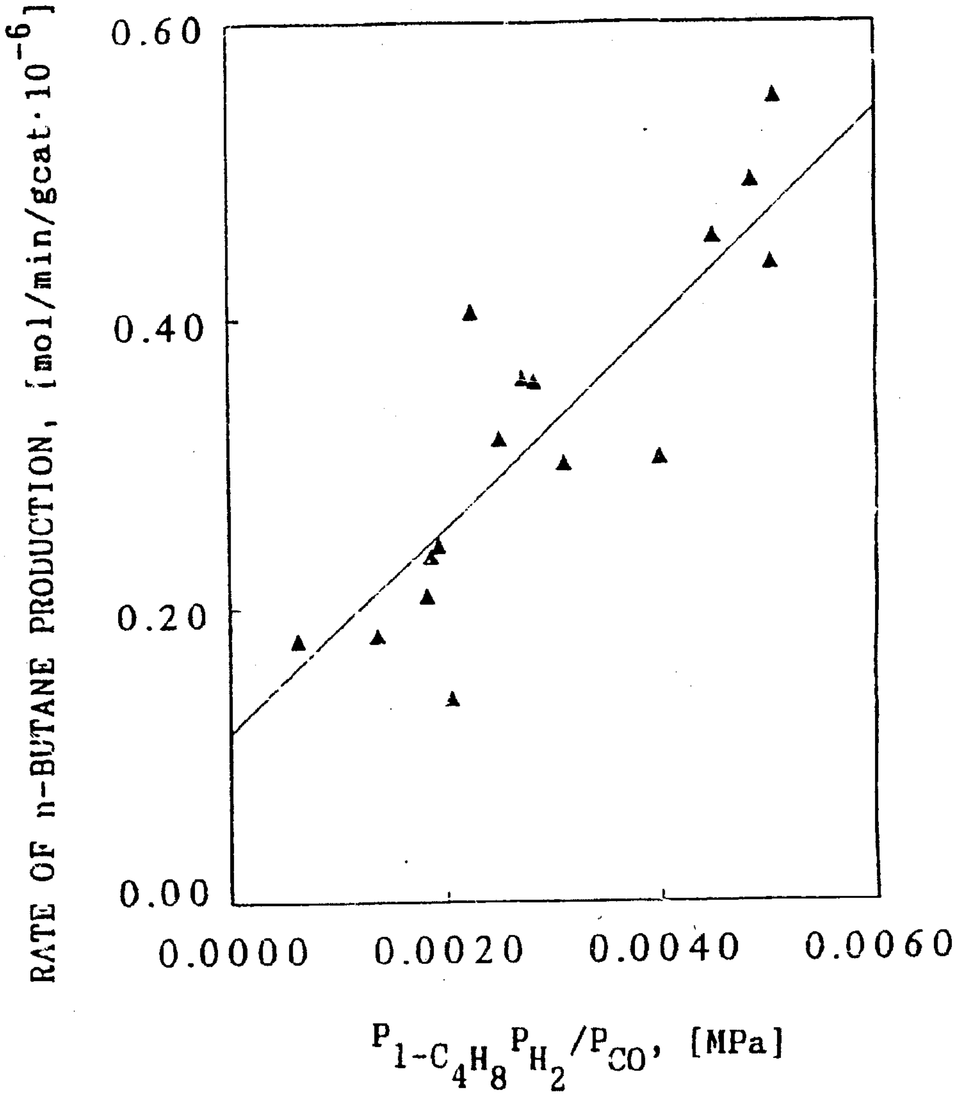

FIGURE 12a. Rate of n-butane production following a simple hydrogenation model at 220°C.

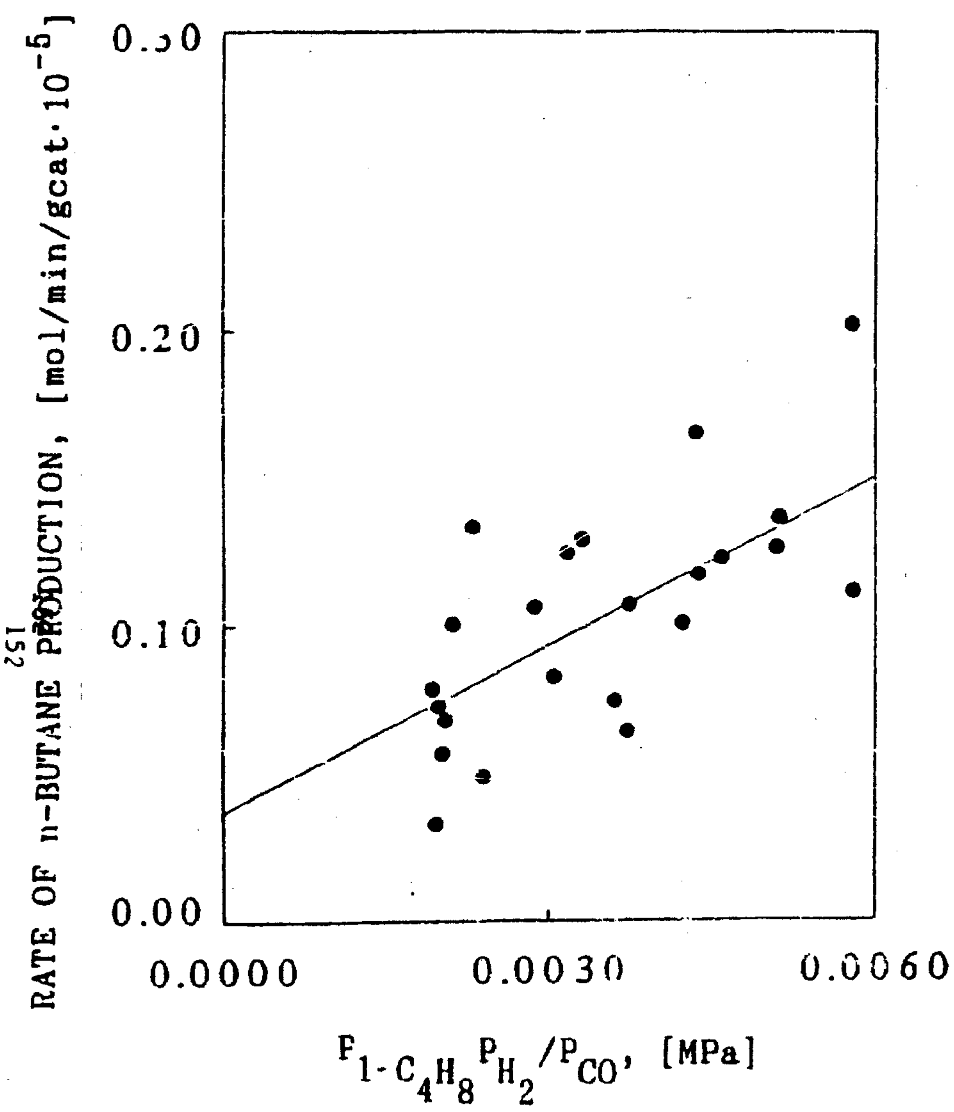

FIGURE 12b Rate of n-butane production following a simple hydrogenation model at 240°C.

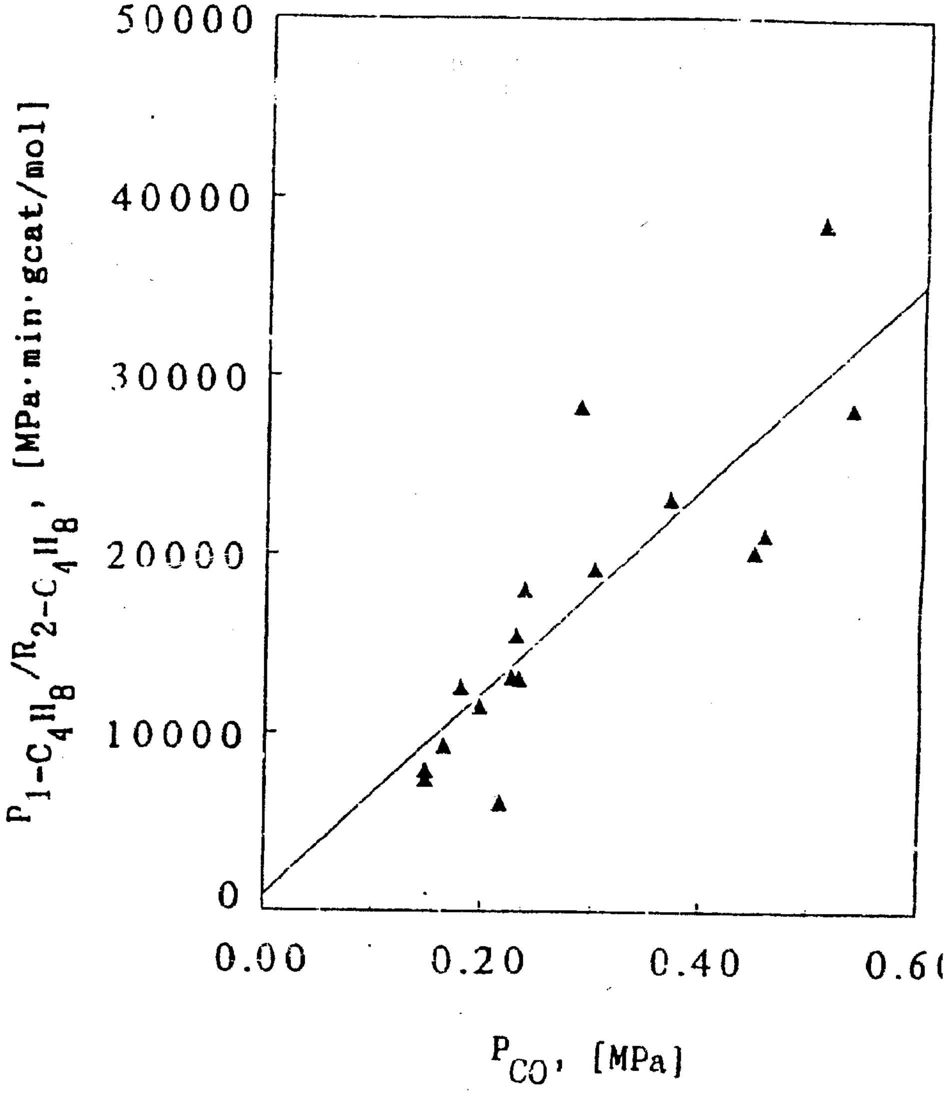

FIGURE 13a. Rate of 2-butene production following a simple isomerization model at 220°C.

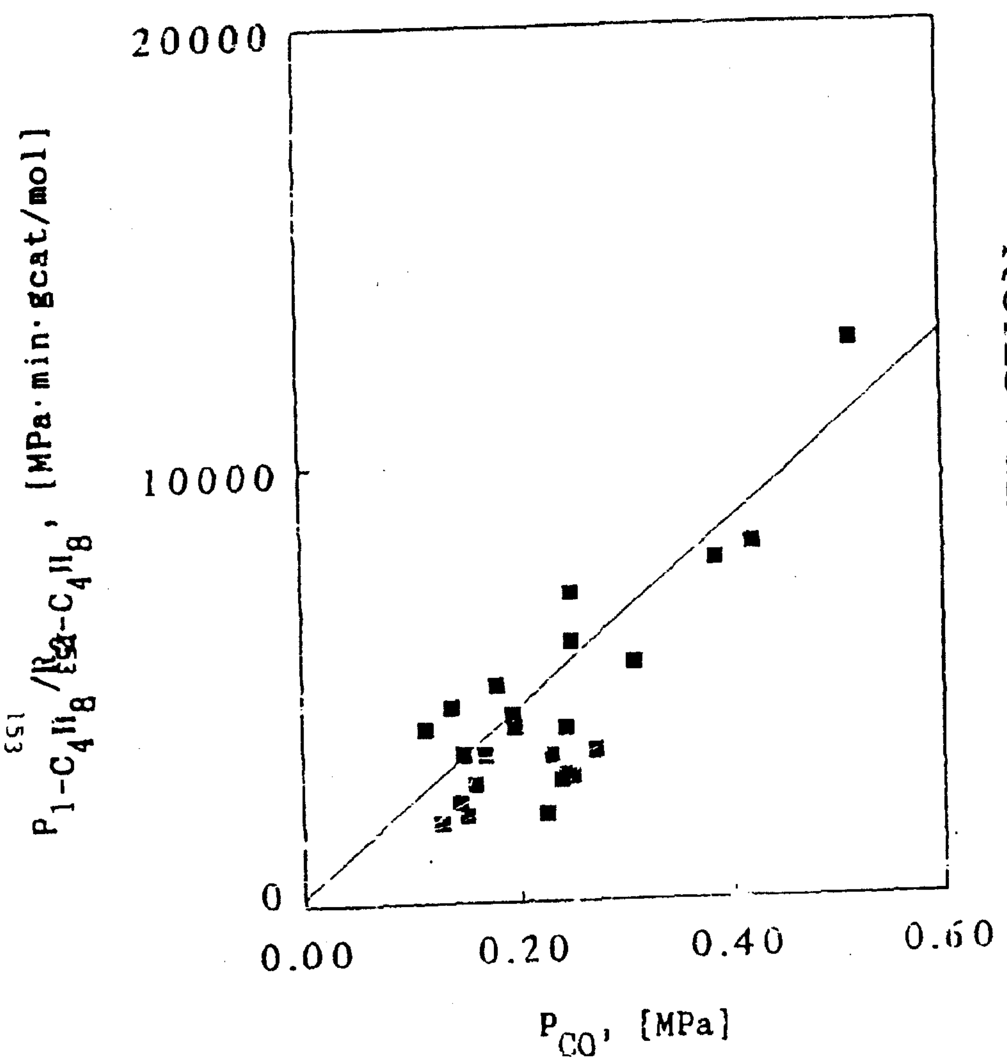

FIGURE 13b. Rate of 2-butene production following a simple isomerization model at 240°C.

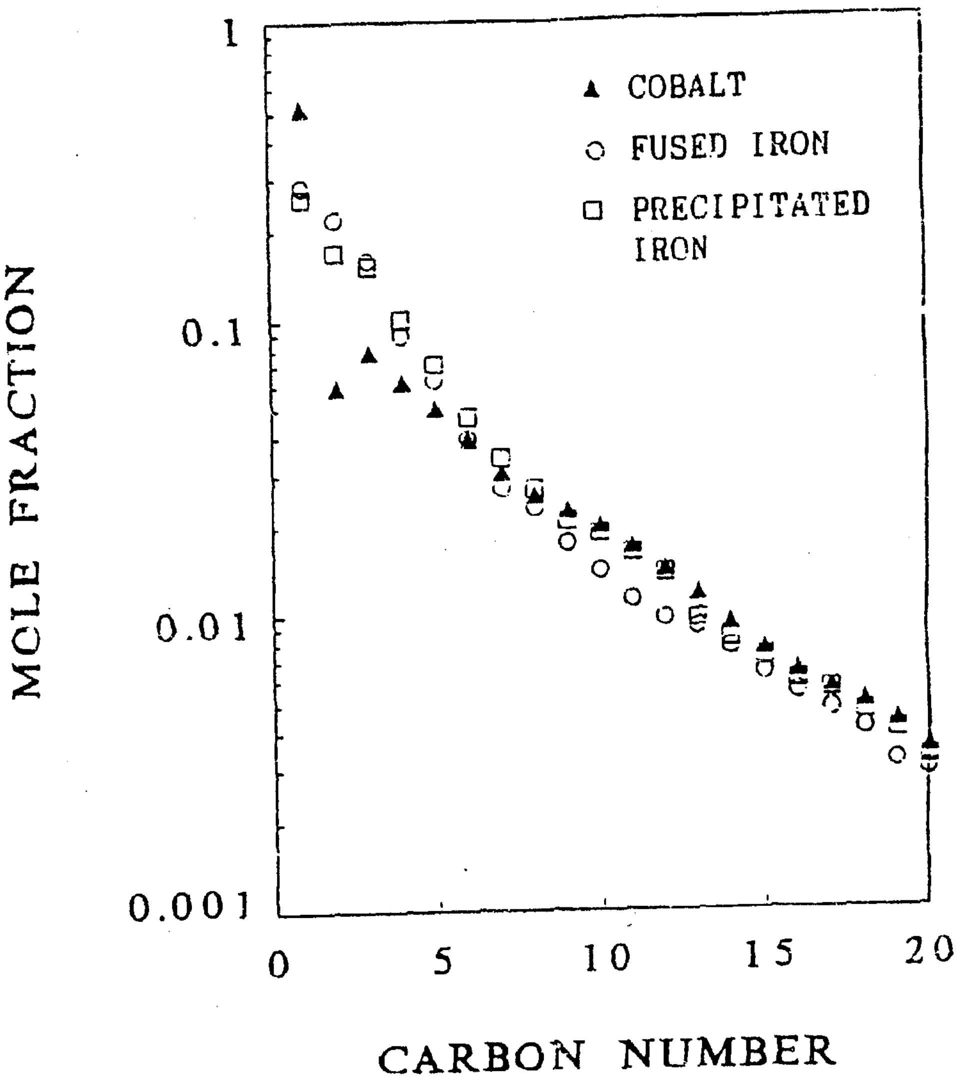

FIGURE 14. Comparison of typical Schulz-Flory diagrams from cobalt (this study), fused iron (C-73, Huff, 1982), potassium- and copper-promoted, precipitated iron (Ruhrchemie, Donnelly and Satterfield, 1989). Co at 240°C, 0.51 MPa, $H_2/CO = 1.86$ syngas.

TABLE 1

COMPARISON OF HYDROCARBON SELECTIVITIES

CATALYST:	COBALT	PRECIPITATED IRON	FUSED IRON
WT. % C_1	0.13	0.07	0.07
WT. % C_2-C_4	0.17	0.25	0.27
WT. C_5-C_9	0.27	0.30	0.24
WT. C_{10}^+	0.43	0.38	0.42

TABLE 2

KINETIC EXPRESSIONS

IRON:

ANDERSON: $$-R = \frac{A\, P_{H_2}\, P_{CO}}{(P_{CO} + B\, P_{H_2O})}$$

HUFF: $$-R = \frac{AB'\, P_{H_2}^{\;2}\, P_{CO}}{(B'\, P_{CO}\, P_{H_2} + P_{H_2O})}$$

FOR CONVERSIONS BELOW ABOUT 60%, BOTH REDUCE TO:

$$-R = A'\, P_{H_2}$$

COBALT:

$$-R = \frac{A\, P_{CO}\, P_{H_2}}{(1 + B\, P_{CO})^2}$$