DE91018065

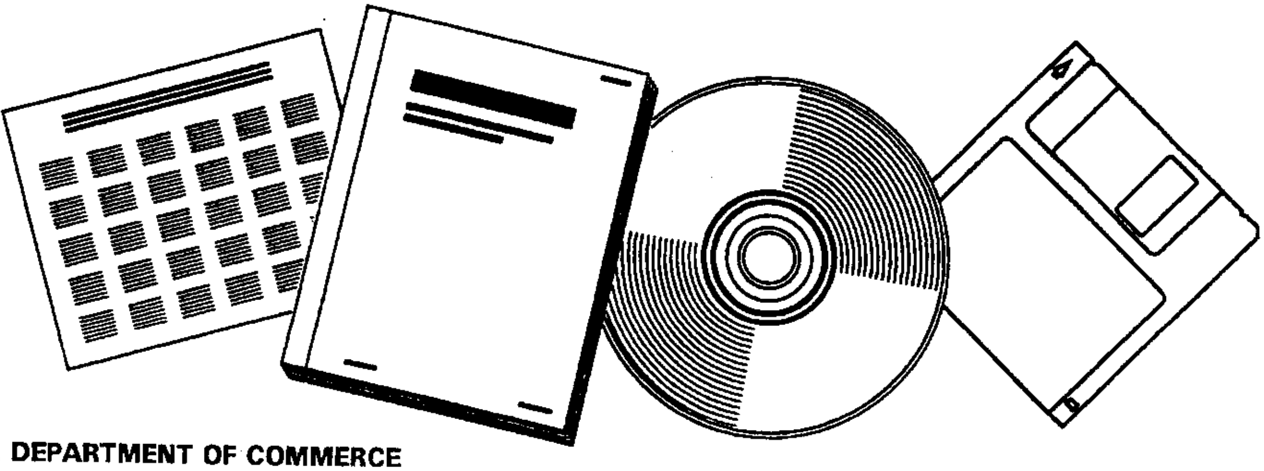
79816-T1

NTIS®
Information is our business.

HYDROCARBON SELECTIVITY OF COBALT FISCHER-TROPSCH CATALYSTS

MASSACHUSETTS INST. OF TECH., CAMBRIDGE.
DEPT. OF CHEMICAL ENGINEERING

JUL 1991



U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

DOE/PC/79816-T1
(DE91018065)
Distribution Category UC-108

THE HYDROCARBON SELECTIVITY OF COBALT FISCHER-TROPSCH CATALYSTS

By
Ian C. Yates
Charles N. Satterfield

July 1991

For
U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania
By
Massachusetts Institute of Technology
Cambridge, Massachusetts

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA 22161

The Hydrocarbon Selectivity of Cobalt Fischer-Tropsch Catalysts

by

Ian C. Yates

and

Charles N. Satterfield*

Department of Chemical Engineering

Massachusetts Institute of Technology

Cambridge, MA 02139

Abstract

A cobalt Fischer-Tropsch catalyst was studied in a continuous-flow, well-stirred slurry reactor at 220 to 240°C, 0.5 to 1.5 MPa, H_2/CO feed ratios between 1.5 and 3.5, H_2 conversions between 6 and 68%, and CO conversions between 11 and 73%.

Increasing space velocity (decreasing conversion) or decreasing reactor H_2/CO ratio decreased the yield of (undesired) C_1 products and increased the yield of (desired) $C_{10}+$ products. Reactor temperature and pressure had little effect on the carbon number distribution. These findings are interpreted in terms of the extent of the readsorption of 1-alkenes into growing chains on the catalyst surface. The relative selectivity to 1-alkenes by the primary synthesis and secondary reaction of 1-alkenes to n-alkanes and 2-alkenes depends on reactor H_2/CO ratio and CO concentration.

Introduction

The chemistry of the Fischer-Tropsch synthesis can be described as the polymerization of single-carbon units on a catalytic site.[1-3] The distribution of products may be characterized by a parameter α, the Schulz-Flory chain growth probability; in its simplest formulation α is the likelihood that a C_n species on the catalyst surface will add another carbon and become a C_{n+1} species, rather than desorb as a product. More than one chain growth probability may exist. The existence of product distributions with two chain growth probabilities, α_1 for low carbon numbers and α_2 for high carbon numbers, has been observed experimentally on iron catalysts by many investigators[4-7] and has been reported also for cobalt in a study by Schulz.[8]

On iron-based Fischer-Tropsch catalysts, a sharp "break" from α_1, with a value usually near 0.6, to α_2, having a higher value, usually near 0.9, occurs on a semi-logarithmic plot of mole fraction versus carbon number, typically at about C_{10}. The double-α and its mathematical development are discussed in detail by Donnelly et al.[3] Data from previous studies indicate that the break from α_1 to α_2 may be less pronounced on cobalt catalysts than on iron catalysts.

The objective of this study was to characterize the hydrocarbon selectivity on a cobalt Fischer-Tropsch catalyst as a function of process variables over a wide range of industrially-relevant conditions. Particular attention was paid to understanding the effects of process variables on the yield of desired high-molecular weight products.

The secondary reactions of 1-alkenes can have a significant effect on the observed product distributions on cobalt. 1-Alkenes can incorporate into growing chains, the extent of which is affected by competitive reactions, largely alkene hydrogenation and isomerization to the 2-alkene. The effects of 1-alkenes deliberately added during synthesis on the product distribution on cobalt catalysts will be discussed in an accompanying paper,[9] together with relevant literature.

Literature Review

Reports on hydrocarbon distributions from cobalt catalysts date back to the early days of the Fischer-Tropsch synthesis in Germany, in which cobalt was used in industrial plants during World War II. Results from this early German work and other studies immediately following World War II are summarized by Storch et al.[10] On the $Co/ThO_2/MgO$/kieselguhr catalysts studied, the selectivity to heavy products increased with decreasing H_2/CO ratios, and reportedly went through a maximum with respect to pressure between 0.5 and 0.85 MPa and remained unaffected by conversion. From a considerable number of more recent studies, we comment only on those most closely related to our work. Product distributions can be affected by many variables such as operating pressure, temperature, degree of conversion, H_2/CO ratio, catalyst composition, and nature of reactor, such as integral fixed bed versus a well-mixed flow reactor. Thus some reported results may seem to be contradictory.

Borghard and Bennett[11] studied a 34 wt.% Co/SiO_2 catalyst at 2.03 MPa and 250°C with a H_2/CO feed ratio of 2 in a fixed bed reactor and compared the product distribution with that from several iron catalysts. In differential reactor studies performed at 250°C, atmospheric pressure, and conversions below 2% on a Co/Al_2O_3

catalyst, Rautavuoma and van der Baan[12] report data on the C_1-C_7 hydrocarbon distribution. Values of α varied from 0.49 to 0.82. Beuther et al.[13] 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. The data are somewhat difficult to interpret, but the selectivity to higher hydrocarbons can be inferred to decrease with increasing temperature.

The most extensive results are from a variety of studies by Schulz and co-workers. Some of these appear in rather inaccessible sources and frequently work with cobalt is discussed in conjunction with more extensive studies on iron. The most extensive studies were apparently obtained by Schulz[8] on five different cobalt compositions, all containing ThO_2 and a silica gel support. Three also contained MgO. Reaction conditions were varied from 0.1 to 3.3 MPa, 175 to 210°C and H_2/CO ratios usually of 1.8 to 2.0, utilizing a fixed bed reactor. A double α product distribution is reported, breaking at about $C_{10,}$ attributed to incorporation of olefinic primary products. The carbon number distribution of products varied substantially with operating conditions.

From this study and a later report summarizing much of his work, Schulz et al.[14] drew a number of generalizations. The ratio of alkenes to alkanes decreased with increasing carbon number, increased with increasing pressure and decreased with increasing space velocity (lower conversion). These are basically trends in alkene hydrogenation. Higher molecular weight alkenes are postulated to be more strongly adsorbed, the reduction in hydrogenation at higher pressures is attributed to inhibition of alkene adsorption by increased adsorption of CO. At high space velocities (low conversion) increased hydrogenation is attributed to higher hydrogen pressure.

Hydrogenation increased with increasing temperature, which can also be interpreted in terms of competitive adsorption of CO, that would be expected to decrease at higher temperatures. Methane selectivity was reported to be in the range of 7 to 14 carbon% (% of total C in hydrocarbon products, qualitatively very similar to wt.%) and increased with increasing temperature. The formation of 2-alkenes was lower at low conversions, and decreased with increasing pressure and temperature. The isomerization of 1-alkenes to 2-alkenes increased with increasing carbon numbers, possibly as a result of longer residence times of higher-molecular weight 1-alkenes.

Operating with a Berty reactor at 250°C, Sarup and Wojciechowski[15] examined the effect of H_2/CO ratio on product distribution over a Co/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 decreased with increasing H_2/CO ratio.

Fu et al.[16] studied 10 and 15 wt.% Co on Al_2O_3 at 0.1 MPa in a differential reactor. Temperature was varied from 200°C to 235°C, H_2/CO ratios from 0.5 to 3, and a four-fold range of space velocities was examined. Selectivities are reported in terms of C-number ranges, the highest being $C_{12}+$. The resulting α_1 values varied from about 0.6 to 0.8. Chain growth probability decreased with increasing inlet H_2/CO ratio and increasing temperature.

Experimental

The experiments were performed in a continuous, mechanically-stirred, one-liter autoclave. The slurry reactor and ancillary equipment are described in detail elsewhere.[17,18] The reactor and its contents are well-mixed and the reactor operates free of heat and mass transfer limitations.[17,19] The fact that data can be obtained at uniform temperature and composition facilitates interpretation, in contrast to difficulties that may be encountered with data from a fixed bed reactor.

The reactor was initially charged with 400 g of n-octacosane, that had been previously recrystallized in tetrahydrofuran (HPLC grade, >99.9% purity) to remove a bromine impurity.[17] The catalyst was prepared by an outside facility and is of the approximate composition of the cobalt catalysts used at Ruhrchemie.[10] The nominal composition, as reported to us by its manufacturer, is 21.4 wt.% Co (as Co), 3.9 wt.% Mg (as Mg), and the remainder diatomaceous earth.

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 a 7 μm frit 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 4.75 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 held at 330°C for 0.75 hours and subsequently the unit was pressurized 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.).

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 inlet $H_2/CO=2.0$ 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.[20,3] For data acquisition reactor temperature was varied between 220 and 240°C. Pressure was varied from 0.5 to 1.5 MPa and H_2/CO feed ratios from 1.5 to 3.5. By changing space velocity between 0.085 and 0.008 Nl/min/gcat (unreduced basis) total synthesis gas conversions were varied from 11 to 70%.

Material balances 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, were condensed in two traps, one kept at 85°C and reactor pressure, the other at 1°C and 0.34 MPa. Material balances included in the analyses were required to close between 97 and 103% on oxygen for acceptance. This was chosen as the material balance closure criterion because carbon and hydrogen accumulate in the reactor in the form of waxes.[3,20]

Products were analyzed with three gas chromatographs, as described by Huff et al.[20a] 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 two product 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 thermal conductivity detector (TCD) and glass column packed with 60/80 mesh Tenax. 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.

Hydrocarbon Carbon Number Distributions

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. The results presented here focus on the effects of process variables on the hydrocarbon product distributions of the synthesis. Particular attention was 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 to operating conditions, the secondary reactions of synthesized 1-alkenes were also examined.

Representative Product Distributions. Figures 1 and 2 show representative Schulz-Flory diagrams of products volatilized from the reactor. The C_3+ data are well described by a double-α Schulz-Flory model. The solid line in Figures 1 and 2 is the best-fit nonlinear regression of a double-α model as developed by Donnelly et al.[3] Above about C_{15}-C_{20}, the overhead product distribution deviates increasingly from that actually formed because of retention of heavy products in the reactor.

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 about 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.[20,21,22] For a description of this two-site interpretation of the double-α, see [4,20,22].

Figure 3 shows a Schulz-Flory diagram of a wax sample taken from the reactor slurry at the end of the run. The value of α_2 estimated by linear regression of the data between C_{30} and C_{53} was 0.87. Although this sample represents the sum of all product distributions from the entire run, note that this value of α_2 is close to that calculated by the nonlinear regression from the overhead products. The asymptotic linear relationship holds over a wide range of carbon numbers, indicating that chain growth probability reaches a constant value at high carbon numbers.

The Effect of Operating Parameters. A useful method of reporting results on product distributions is to report α_1, α_2, and either Ω, the breakpoint between the two distributions, or x_1, the product fraction formed by the α_1 distribution. In addition, we determine respective 95% confidence intervals or standard deviation of parameter estimate. However, Ω or x_1 is difficult to estimate precisely from regression of experimental data and therefore, an additional method of reporting selectivity data is useful. Because of low volatility, products at higher carbon numbers tend to 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.

The recommended method used here is as follows. First, the data from C_3 to C_N are fit and estimates of α_1, α_2, and Ω made. Second, the mole fractions from C_N to C_{100} are extrapolated and used to generate estimates of the "data" in terms of weight fractions. Assuming that all products above C_N have the molecular weight of alkanes is generally reasonable; however, if more precise estimates about the within-carbon-number selectivity are known, these can be included also. Third, the actual weight of products produced at C_1 and C_2 are included and the data are then expressed in terms of weight classes. Weight classes which are industrially-relevant are C_1, C_2-C_4 (light gas), C_5-C_9 (gasoline), and C_{10}+ (diesel and wax). Finally, to check that the estimate of the weight classes is reasonable, the closure on carbon, including the extrapolated hydrocarbons, is estimated and required to fall between 95 and 105%.

By expressing the data in terms of these weight classes, minor differences in the nonlinear regression results will have less tendency to mislead interpretation of the data and selectivity correlation. For example, in some analyses α_2 may seem slightly high, while Ω may be also be high; thus, it is impossible to determine which conditions are better by examining the effect of process conditions on α_2 only. To simplify presentation of the results here, only C_1 and $C_{10}+$ products are reported. These two product classes are representative of undesirable and desirable products, respectively.

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 near the usage ratio of cobalt and therefore varying space velocity has little effect on reactor H_2/CO. Increasing space velocity (decreasing conversion) increases the fraction of $C_{10}+$, while decreasing the yield of C_1 products.

One possible interpretation is that at higher conversions, a product, such as water, might readsorb onto the surface of the catalyst and increase chain termination. However, the effect seems to be related rather to the extent of chain incorporation of 1-alkenes relative to being hydrogenated or isomerized to 2-alkenes. At higher space velocity (lower residence time), 1-alkenes are hydrogenated or isomerized less than at lower space velocities because of the decrease in residence time of the 1-alkenes.

Pressure. 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 remained constant over a range of total reactor pressure of 0.5 to 1.5 MPa. In a study at 175°C, and pressures of 0.12 to 3.3 MPa, using a (H_2/CO) inlet ratio of 1.8, Schulz[8] reported that methane selectivity decreased with increasing pressure. The $C_{10}+$ product distribution scattered considerably with pressure. The (H_2/CO) exit ratio was nearly constant, in the range of 1.6 to 1.7.

Temperature. Figure 6 shows the dependence of the weight fractions of C_1 and $C_{10}+$ for total synthesis gas conversions between 31 and 33% at 220 and 240°C. Data are presented at comparable conversion, rather than equivalent space velocities, because the ratio of product to reactant concentration appears to have a marked effect. No trend is observed over this limited temperature range. In a study at 1.7 MPa and 170 to 190°C, using a (H_2/CO) inlet ratio of 1.0, Schulz[8] reported that methane formation increased with temperature but there was little effect of temperature on the $C_{10}+$ distribution. However the exit (H_2/CO) ratio varied substantially through the reactor. The exit value decreased from 0.65 at 170°C to 0.24 at 190°C.

Reactor H_2/CO Ratio. Figure 7 shows the effect of reactor H_2/CO ratio on the relative yield of C_1 products at 220°C. Similar plots were generated showing the analogous trends at 230 and 240°C[23] but are not shown here. Increasing reactor H_2/CO ratios increases the relative weight fraction of C_1 at all temperatures, although the trend is more apparent at lower temperatures. 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, as is examined below.

Figure 8 shows the effect of reactor H_2/CO ratio on the fractional yield of products in the $C_{10}+$ range at 220°C. Again, similar plots were generated showing the analogous trends at 230 and 240°C,[23] but are not shown here. Increasing reactor H_2/CO ratio decreases the yield of high-molecular weight products relative to total hydrocarbons synthesized. This decrease can be primarily attributed to the increase in rate of production of low-molecular weight products, particularly methane. This general trend has also been reported by others.[8,11,16]

Selectivity to Various Product Classes

Figures 9 and 10 show component Schulz-Flory diagrams including the distribution of three major product classes, n-alkanes, 1-alkenes, and n-alcohols. Three other component were observed in much lower concentrations than these at each carbon number; in order of relative abundance, they were 2-alkenes, branched alkanes, and aldehydes (only at C_2 and C_3 and 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.[3] The observed C_2 concentration on cobalt is generally less than on iron.[8]

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. Above C_3, the fraction of synthesized products which are hydrogenated increases with increasing carbon number.

In contrast to n-alkanes and n-alcohols, 1-alkenes appear to follow a single-α type distribution in Figures 9 and 10. The extent to which observed products represent the primary synthesis versus secondary reactions varies depending on reactor conditions. 1-

alkenes, presumed to be the primary product of the synthesis by Schulz et al.,[14] may be hydrogenated to n-alkanes or isomerized to 2-alkenes. The ratio of 1-alkene/n-alkane and 1-alkene/2-alkene both decrease with increasing carbon number, as was also observed by Schulz[8] and Rautavuoma and van der Baan.[12] As shown below, a large fraction of n-alkanes appear to be produced by the hydrogenation of 1-alkenes. Therefore, assuming independent mechanisms for the production of 1-alkenes and alkanes, based on differences in component Schulz-Flory diagrams, may be incorrect.

Since the formation of C_1 products appeared markedly different from the formation of other components, we examined the fit of the rate expression developed elsewhere for the consumption of synthesis gas to the formation of C_1 and C_2+ products as two separate groups. The expression is[24]:

$$-R_{H_2+CO} = \frac{aP_{CO}P_{H_2}}{(1 + bP_{CO})^2} \tag{1}$$

Figure 11 shows that the rate of C_1 formation is well fit by the linearized form of equation 1. Figure 12 shows that the rate of C_2+ formation is also well fit by equation 1. Thus, the decrease in yield of higher molecular weight products with increasing H_2/CO does not seem to result from competing rate mechanisms for formation of C_1 versus C_2+ products.

Secondary Reactions of 1-Alkenes

In characterizing secondary reactions, the rate of formation of ethane, n-butane, and 2-butene were studied. Ethane represents hydrogenation only; the behavior of the C_4 compounds is taken as representative of that of the C_3+ products. As discussed by Hanlon and Satterfield,[25] and Donnelly and Satterfield,[7] C_4 products are the highest molecular weight products which do not split between vapor and liquid phases in our traps and therefore are the least subject to experimental error.

Rate of Ethane Formation from Ethene. Figure 13 shows 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; data at 220°C are shown as representative. This assumes that ethane formation is a simple hydrogenation process inhibited by adsorbed CO. While the data scatter somewhat, much of the variation in the rate of ethane formation can be explained by such a simple model. The vertical axis intercept of this figure represents the amount of ethane produced as primary product. 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 14 shows 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; data at 220°C are shown as representative. Again, a simple hydrogenation process inhibited by adsorbed CO is assumed. While there is considerable scatter in the data in Figure 14, the rate of n-butane formation clearly increases with increasing $P_{C_4H_8}P_{H_2}/P_{CO}$. The vertical axis intercept of this figure 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[8,14] and Rautavuoma and van der Baan[12] on cobalt and Donnelly and Satterfield[7] on iron 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 not considered to be a primary product, but are assumed to be produced solely by isomerization of 1-alkenes.[14] Thus a model was developed which accounts for all of the production of 2-butene in terms of 1-butene isomerization. A Langmuir-Hinshelwood-type relationship of the following form is proposed:

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

Equation 2 assumes that the rate of 2-butene formation is simply proportional to the concentration of 1-butene and inhibited by carbon monoxide. Equation 2 can be linearized, yielding

$$\frac{P_{1\text{-butene}}}{R_{2\text{-butene}}} = \frac{1}{k} + \frac{K_{CO}P_{CO}}{k} \tag{3}$$

Following the relationship of equation 3, Figures 15a and 15b depict 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. Data from two temperatures are shown here in order to justify the added complexity of the proposed two-parameter 2-alkene production model.

The conclusion of Schulz et al.[14] that the ratio of 1-alkenes/total alkenes increases with increasing total pressure is consistent with equation 2 since the range of values of (H_2/CO) through his fixed bed reactor was within the range of 1.8 to 1.6 throughout his wide range of pressure.

Summary. Three interesting conclusions can be drawn. First, a large fraction of the alkanes and all 2-alkenes appear to be produced by secondary reactions. Second, increasing the reactor H_2/CO ratio increases the ratio of alkane to 1-alkene at each carbon number. If 1-alkenes readsorb 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