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STUDY OF THE FISCHER-TROPSCH REACTION USING ON-LINE GAS-CHROMATOGRAPHIC ANALYSIS

DEPARTMENT OF ENERGY, PITTSBURGH, PA.
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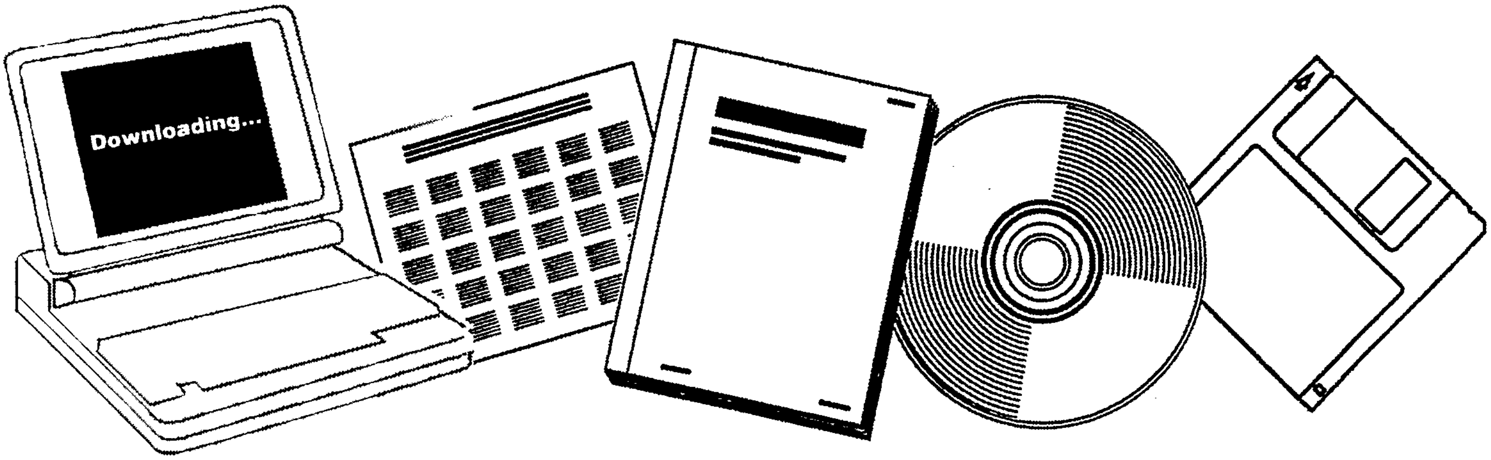

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A STUDY OF THE FISCHER-TROPSCH REACTION USING ON-LINE GAS-CHROMATOGRAPHIC ANALYSIS

Richard A. Diffenbach

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A STUDY OF THE FISCHER-TROPSCH REACTION USING ON-LINE GAS-CHROMATOGRAPHIC ANALYSIS

Richard A. Diffenbach[1], Thomas H. Johnson[2], and
Richard R. Schehl[3]

SUMMARY

An on-line gas-chromatographic method was used to analyze the products obtained during the course of a Fischer-Tropsch reaction. The utility of this method for investigating catalyst activity and selectivity throughout the catalyst lifetime is illustrated. The variation in product composition with different reaction parameters has been demonstrated. The adherence of a classical Fischer-Tropsch iron catalyst to Anderson-Schulz-Flory kinetics can be illustrated under a variety of reaction conditions.

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INTRODUCTION

The advent of the energy crisis has brought renewed interest in the Fischer-Tropsch reaction[1]. Some of the problems associated with the characterization of catalysts for the Fischer-Tropsch reaction included a lack of continuous analysis over a wide range of hydrocarbons and an accurate analysis over the C_4-C_8 fraction. One would like to have the former capability in order to determine catalyst activity and selectivity over a period of time. The difficulty encountered in determining the C_4-C_8 fraction lies in the fact that these hydrocarbons distribute themselves in both the gas and liquid phases. Hence, a measure of this hydrocarbon fraction in either phase represents an incomplete analysis. Additionally, the volatility of this fraction gives rise to partial loss from the liquid phase and further complicates the analysis. An on-line method of analysis, where the product stream was kept in the gas phase from the reactor to the gas chromatograph, seemed like a logical approach to the problem. The details of the analytical method are contained in the Experimental.

In addition to obtaining information on differing hydrocarbon weight fractions, we felt it was desirable to obtain information about 1-olefin/*n*-paraffin ratios within a hydrocarbon fraction. Our interest in this data stems from the knowledge that olefinic compounds serve as precursors to aromatic compounds in zeolite-mediated reactions.[2] The formation of aromatic compounds is important if one hopes to obtain high octane fuels from coal-derived synthesis gas. Additionally, there is some interest in determining if the Fischer-Tropsch product distribution can be altered by adding an olefin to the synthesis gas. If olefins are to be incorporated into the chaingrowth step of the Fischer-Tropsch reaction, then it behooves one to uncover the fate of the olefins formed during the reaction. We report herein upon the distribution of 1-olefins and _n_-paraffins for the C_2-C_{13} hydrocarbon fraction. Our analysis reports upon changes in the 1-olefin/_n_-paraffin ratio for the same carbon number under a variety of reaction conditions. We do not report upon the effect of added olefin feed in this report.

RESULTS AND DISCUSSION

By the use of on-line gas-chromatographic techniques (see Experimental), we were able to distinguish the seven compounds shown in Table I using the thermal conductivity detector and the C_1-C_{20} hydrocarbons using the flame ionization detector (Table II). Compounds such as carbon monoxide and carbon dioxide are not detectable using flame ionization detectors. However, their detection is important if one wants to examine the effectiveness of carbon monoxide conversion for a particular catalyst under specific conditions. If one wants to convert carbon monoxide conversion and hydrocarbon production to a common scale, then one needs a peak in common for both the TCD and FID analysis. In this instance we have three such peaks: methane, ethylene, and ethane. While our concern in this report deals more with hydrocarbon weight fractions and 1-olefin production, we felt it was important to have a method which was versatile enough to determine carbon monoxide conversion as well. The use of a thermal conductivity detector provides for this analysis.

The retention times of the 1-olefins and n-paraffins for the C_2-C_{13} carbon fractions are shown in Table III. The weight fraction for a specific carbon number, W_n, could be determined for C_1-C_{20}. A plot of log W_n/n vs n (carbon number) should provide a straight line if the reaction follows Anderson-Schulz-Flory kinetics as expected for a Fischer-Tropsch reaction. A typical plot is shown in Figure 1. Adherence of a catalyst system to Anderson-Schulz-Flory kinetics allows one to calculate the polymerization probability, p, from both the slope and the intercept from the equation below. The degree of polymerization, D, can be determined from p by the equation D=1/1-p.

$$\log \frac{W_n}{n} = n \log p + \log \frac{(1-p)^2}{p}$$

Using the average value for p, as determined from the slope and intercept, one can back calculate each weight fraction to determine what it should be if the reaction followed an Anderson-Schulz-Flory kinetic scheme exactly. Table IV illustrates both the experimental and calculated weight fractions for the run shown in Figure 1. The value for p determined from the slope for this run was 0.770 while the value for p determined from the intercept was 0.768 for an average value of 0.769. The average degree of polymerization D was 4.33. The experimentally determined values of p, from the slope and intercept, are very close and in some instances were identical when determined from data obtained in this fashion. The data illustrated in Table IV and Figure 1 were taken from a catalyst run that had been operating only 310 min. Without on-line gas-chromatographic analysis, information of this depth and covering this wide a range of carbon numbers would have been very difficult to obtain after so short a time.

Another advantage of this method of analysis is the opportunity to examine the change in catalyst activity over time. For example, Table V shows the change in catalyst activity as demonstrated by changes in p and D over time. These are important experimental parameters as they determine the production of various hydrocarbon fractions. This is illustrated in Table VI for the same time frames. Of particular interest is the gasoline fraction, C_5-C_{11}. It is apparent from the data, that during

TABLE I. RETENTION TIMES FOR COMPOUNDS DETECTED BY THE THERMAL CONDUCTIVITY DETECTOR

Compound	Time (min)
H_2	1.63
CO	15.65
CH_4	22.21
H_2O	23.26
CO_2	26.58
C_2H_4	37.95
C_2H_6	41.06

TABLE II. RETENTION TIMES FOR COMPOUNDS DETECTED BY THE HYDROGEN FLAME IONIZATION DETECTOR

Compound	Time Frame (min)
CH_4	1.62
C_2H_4	1.97
C_2H_6	2.37
C_3H_6	5.06
C_3H_8	5.31
C_4*	8.31-11.01
C_5*	12.05-15.00
C_6*	16.41-18.46
C_7*	18.79-21.80
C_8*	22.55-25.60
C_9*	26.03-28.12
C_{10}*	28.73-30.65
C_{11}*	31.25-33.02
C_{12}*	33.61-34.88
C_{13}*	35.25-36.93
C_{14}*	37.79-38.85
C_{15}*	39.50-40.64
C_{16}*	41.22-42.84
C_{17}*	43.13-43.92
C_{18}*	44.38-45.49
C_{19}*	45.96-47.25
C_{20}*	47.74-49.27

*Retention times for C_n(n=4-20) fractions are given for all C_n compounds which are eluted over the time frame shown.

TABLE III. RETENTION TIMES FOR 1-OLEFINS VS N-PARAFFINS

Carbon Number	Retention Time (min)	
	1-Olefin	n-Paraffin
2	1.97	2.37
3	5.06	5.31
4	9.55	9.92
5	13.79	14.23
6	17.62	18.01
7	21.03	21.41
8	24.19	24.54
9	27.04	27.36
10	29.66	29.95
11	32.10	32.37
12	34.36	34.60
13	36.45	36.66

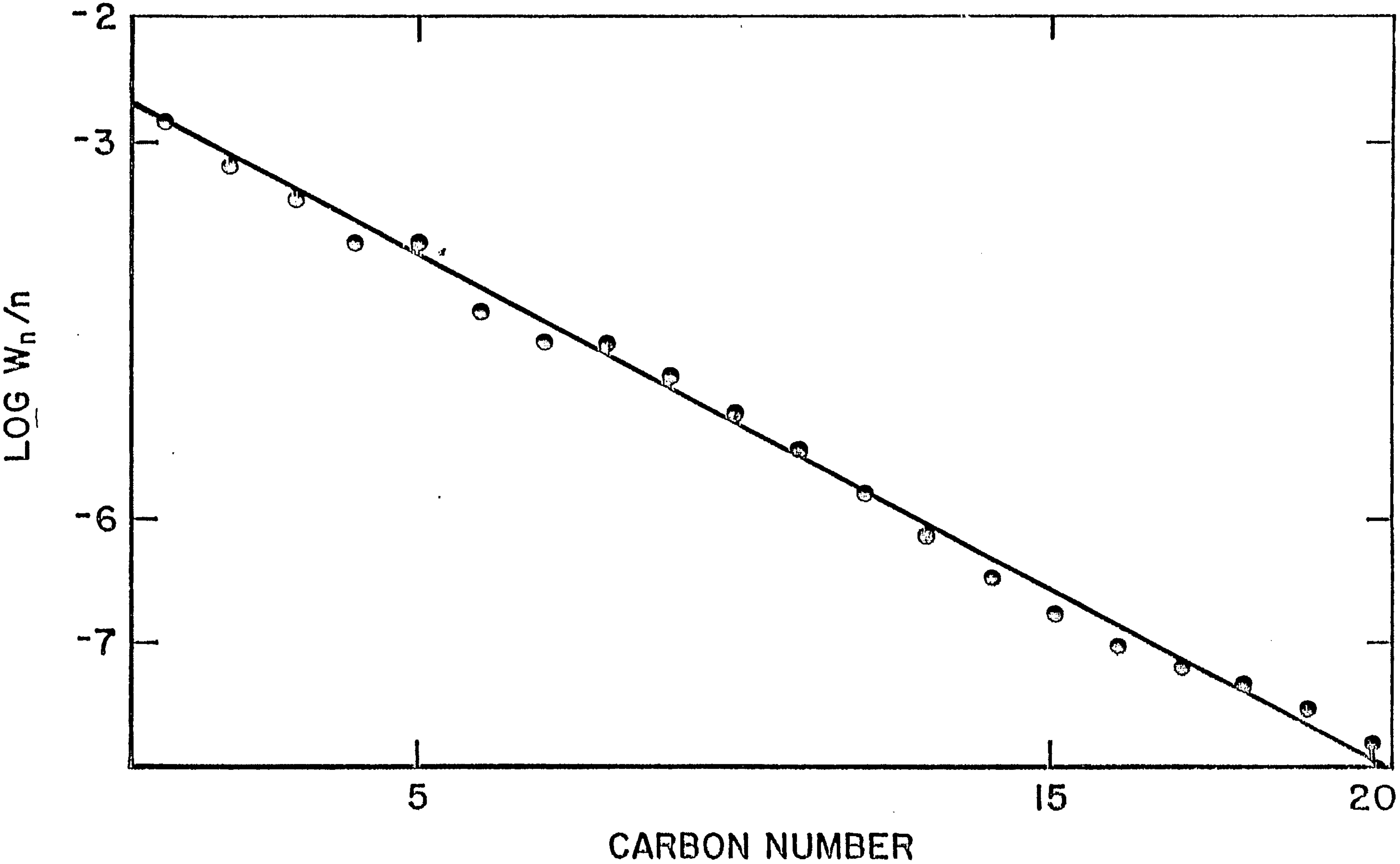

Figure I– Experimental product distribution by carbon number.

the earlier part of the catalyst life, that a higher than predicted amount of gasoline is obtained whereas later stages in the catalyst life give lower quantities of gasoline.

We were interested in knowing if the 1-olefin/n-paraffin ratios obtained from a catalyst were consistent throughout the catalyst's lifetime or if they changed. In order to examine this we determined the 1-olefin/n-paraffin ratios for C_2-C_{13} at four different times. The results are shown in Table VII.

Several trends are apparent from the data reported in Table VII. First, the 1-olefin/n-paraffin ratio seems to change little in the first 22 hours of reaction. However, beginning with data taken at 43 hours, the 1-olefin/n-paraffin ratio decreases significantly for all carbon numbers examined. After 120 hours, this ratio has decreased appreciably. This aspect of the investigation would seem to indicate that the longer a catalyst is on stream, the greater the amount of n-paraffin one will obtain. It would also seem to indicate that the character of the catalyst is changing with time in that it has an apparent increase in hydrogenation activity. This increased hydrogenation activity however is most pronounced for the C_2 fraction which experienced a 37% decrease in the 1-olefin/n-paraffin ratio. Most of the other fractions experienced decreases in this ratio of 20-27% with the exception of the C_{11} fraction (30% decrease) and the C_{13} fraction (35% decrease). This is not the only anomaly expressed by the C_2 fraction. Perusal of the figures in Table VII would indicate a decline in the 1- olefin/n-paraffin ratio from C_3-C_{13} regardless of when this ratio was determined in the catalyst lifetime. Again, C_2 does not fit

TABLE IV. COMPARISON OF EXPERIMENTAL AND CALCULATED WEIGHT FRACTIONS BY CARBON NUMBER*

Carbon Number	W_n (Expt)	W_n (Calc)
1	0.0579	0.0533
2	0.0823	0.0820
3	0.0945	0.0946
4	0.0866	0.0970
5	0.1106	0.0933
6	0.0756	0.0861
7	0.0709	0.0772
8	0.0806	0.0679
9	0.0701	0.0587
10	0.0586	0.0502
11	0.0486	0.0425
12	0.0365	0.0356
13	0.0286	0.0297
14	0.0222	0.0246
15	0.0179	0.0203
16	0.0146	0.0166
17	0.0134	0.0136
18	0.0123	0.0111
19	0.0106	0.0090
20	0.0085	0.0073

*CCI catalyst, reaction temperature 300°C, reaction pressure 300 psig, $H_2/CO = 3:1$, GHSV: 3600 (v/w)h^{-1}

TABLE V. CHANGE IN AVERAGE DEGREE OF POLYMERIZATION WITH TIME*

Time (min)	P	D
310	0.769	4.33
1354	0.768	4.31
1828	0.762	4.21
2510	0.752	4.04

*CCI catalyst, reaction temperature 300°C, reaction pressure 300 psig, $H_2/CO = 3:1$, GHSV: 3600 (v/w)h^{-1}

TABLE VI. CHANGE IN HYDROCARBON DISTRIBUTION WITH TIME*

		Weight Percent	
Time (min)	C_1-C_4 (calc)**	C_5-C_{11} (calc)**	C_9-C_{20} (calc)**
310	32.13(32.69)	51.50(47.59)	34.19(31.92)
1354	36.71(32.93)	47.45(47.60)	29.34(31.68)
1828	36.16(34.04)	48.97(47.62)	31.30(30.63)
2510	40.78(42.39)	46.31(47.49)	26.01(28.55)

*CCI catalyst, reaction temperature 300°C, reaction pressure 300 psig, $H_2/CO = 3:1$, GHSV: 3600 (v/w)h^{-1}

**Values in parenthesis represent theoretically calculated values as obtained from experimentally determined p values.

into this trend. The C_2 fraction starts out with a high paraffin composition whereas the other low hydrocarbons have a high olefin content. In fact, the olefin composition in the C_2 fraction is far more similar to that for the higher hydrocarbons, e.g. C_{12} and C_{13}.

The anomalies observed for the C_2 fraction would seem to suggest that something different is occuring with the C_2 fraction than with the higher C_n fractions. One possibility might be that ethylene is cracking, with hydrogenation to methane, rather than merely hydrogenating to ethane. Both processes could be taking place simultaneously. From a practical standpoint, this should result in a decrease in the C_2 weight fraction and an increase in the C_1 weight fraction. The Anderson-Schulz-Flory plots for the four time frames in Table VII are illustrated in Figures 2-5. It is apparent that a high C_1 weight fraction concurrent with a low C_2 weight fraction does not occur for the four cases in question. A somewhat high C_1 weight fraction occurs in Figure 5 (120h run), but the C_2 weight fraction is quite normal.

While it is true that the hydrogenation of ethylene to ethane is more thermodynamically favored for ethylene than for the other C_n fractions, it is clear that the differences observed here are not merely due to thermodynamic considerations. In a distribution of 1-olefins and n-paraffins controlled solely by thermodynamics, one would observe n-paraffins as the major products for all of the C_n fractions and the 1-olefin/n-paraffin ratios for C_5-C_{13} would be identical as their free energies of hydrogenation are identical. Experimentally, neither of these statements is true.

TABLE VII. CHANGE IN 1-OLEFIN/n-PARAFFIN RATIOS WITH TIME[a]

Carbon Number[b]	Time (h)	1-Olefin/n-Paraffin
C_2	5	0.57
	22	0.52
	43	0.43
	120	0.27
C_3	5	2.92
	22	2.62
	43	2.45
	120	1.83
C_4	5	2.92
	22	2.83
	43	2.44
	120	1.77
C_5	5	2.43
	22	2.39
	43	1.99
	120	1.56
C_6	5	1.86
	22	1.77
	43	1.45
	120	1.10
C_7	5	1.51
	22	1.50
	43	1.20
	120	0.96
C_8	5	1.33
	22	1.32
	43	1.05
	120	0.82
C_9	5	1.21
	22	1.20
	43	0.96
	120	0.75

TABLE VII. CHANGE IN 1-OLEFIN/n-PARAFFIN RATIOS WITH TIME[a], (Cont.)

Carbon Number[b]	Time (h)	1-Olefin/n-Paraffin
C_{10}	5	0.96
	22	0.96
	43	0.77
	120	0.57
C_{11}	5	0.84
	22	0.84
	43	0.67
	120	0.47
C_{12}	5	0.53
	22	0.55
	43	0.43
	120	0.32
C_{13}	5	0.46
	22	0.45
	43	0.34
	120	0.22

[a] Conditions: reaction temperature 300°C, reaction pressure 300 pisg, GHSV: 3600 (v/w)h^{-1}, H_2/CO = 3:1

[b] For example, C_2 is ethylene/ethane, C_3 is propylene/propane, etc.

It is intriguing to speculate on not only why the C_2 fraction does not follow the pattern of 1-olefin/n-paraffin ratios exhibited by the C_3-C_{13} fractions, but why the pattern of increasing n-paraffin with increasing carbon number exists at all. We have already seen that thermodynamic considerations do not hold the answer. From steric considerations, one could speculate that lower hydrocarbons should be more enriched with n-paraffin than olefin and that olefins would dominate at higher carbon numbers. However, one observes the opposite trend with this catalyst.

A possible explanation for the increased amount of n-paraffin in higher carbon numbers could be related to the higher boiling points of the higher molecular weight olefins. In other words, lower boiling components may have a shorter contact time with the catalyst than higher boiling components. Lower n-paraffin content would be a logical consequence of this boil off. In order to assess this possibility we have plotted the 1- olefin/n-paraffin ratios vs the boiling points of the 1-olefins in Figure 6. The most dramatic observation in Figure 6 is the total lack of adherence by the C_2 fraction to this boiling relationship. The other C_n fractions seem to show a relationship between boiling point and the 1-olefin/n-paraffin ratio; however, the C_4 and C_5 fractions appear to be high in 1-olefin content in this relationship. One might be able to argue that compounds boiling as low as 1-butene and 1-pentene do not adhere closely to this relationship because of the extreme difference between the reaction temperature and their boiling points. However, propylene which has an even lower boiling point seems to fit the relationship rather well.

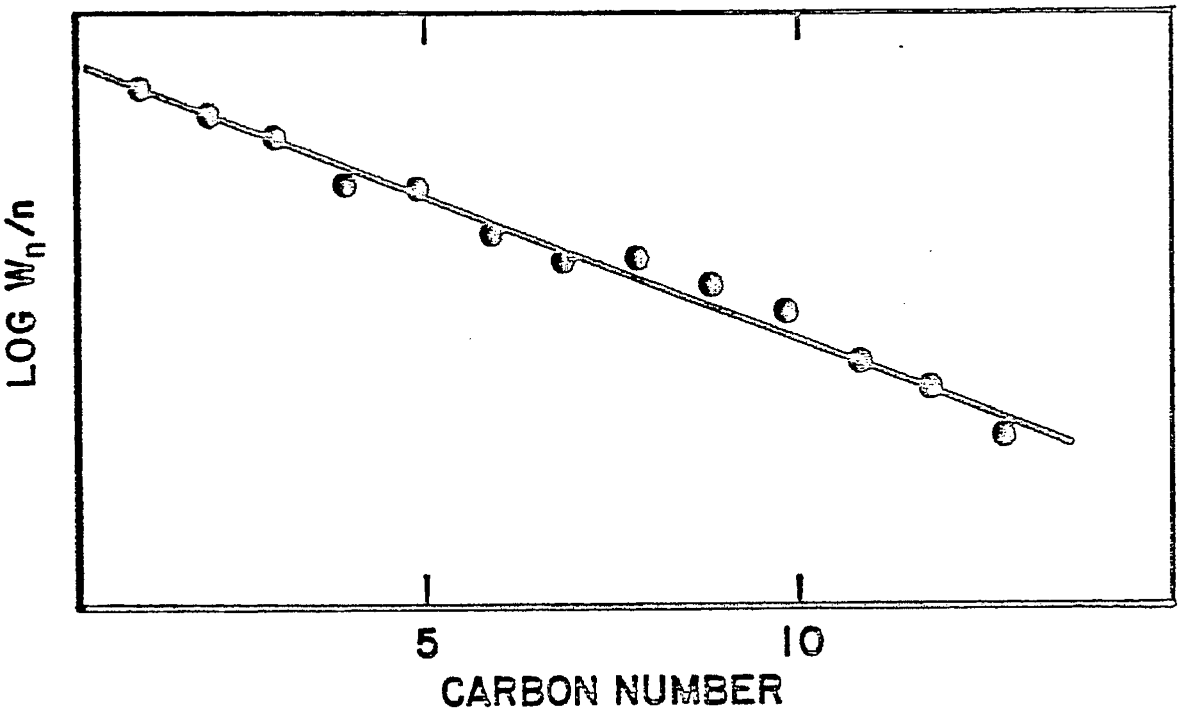

Figure 2-Anderson-Schulz-Flory plot for 5h reaction, Table I.

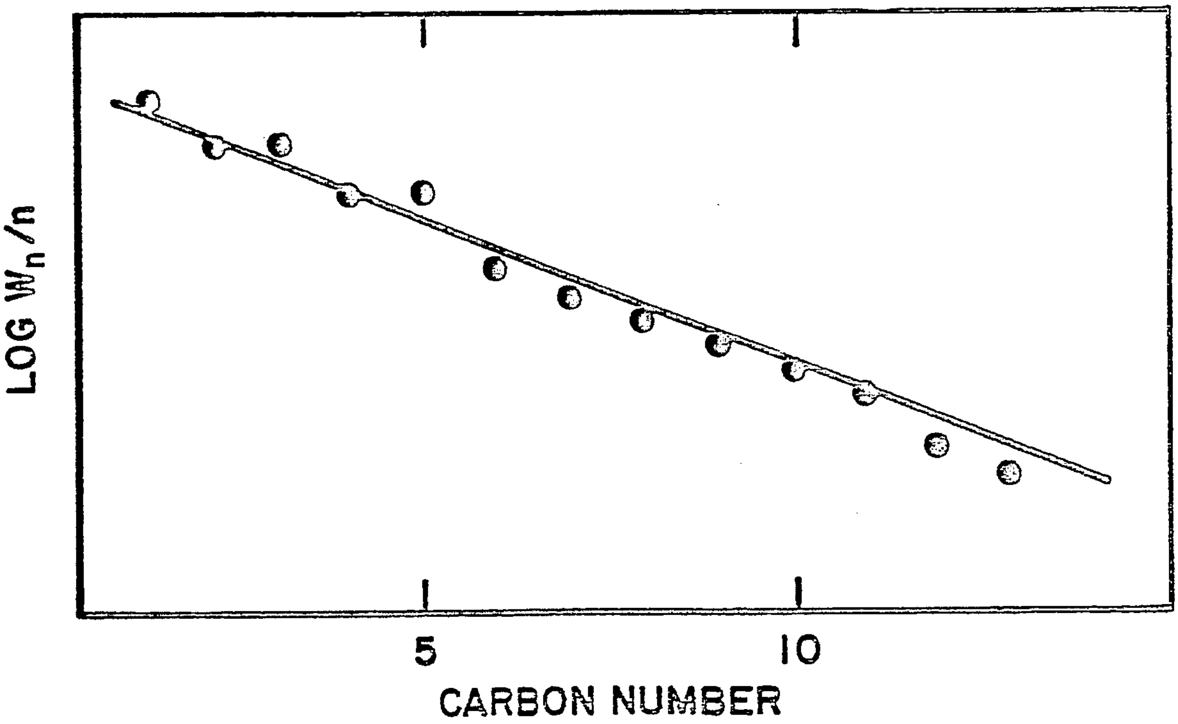

Figure 3-Anderson-Schulz-Flory plot for 22h reaction, Table I.

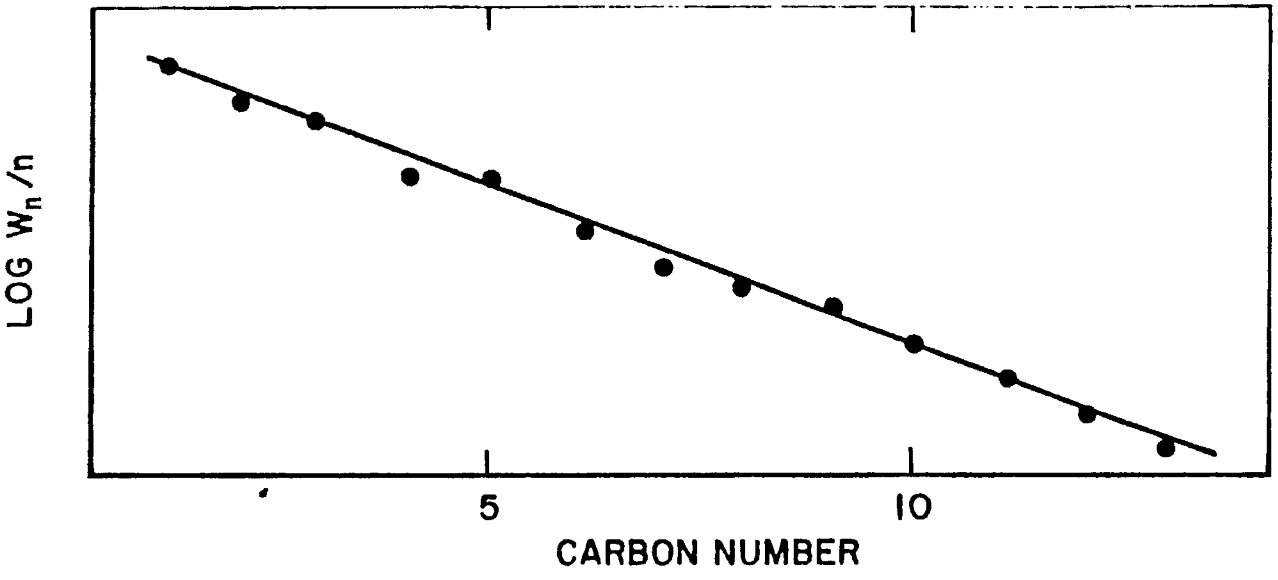

Figure 4- Anderson-Schulz-Flory plot for 43h reaction, Table I.

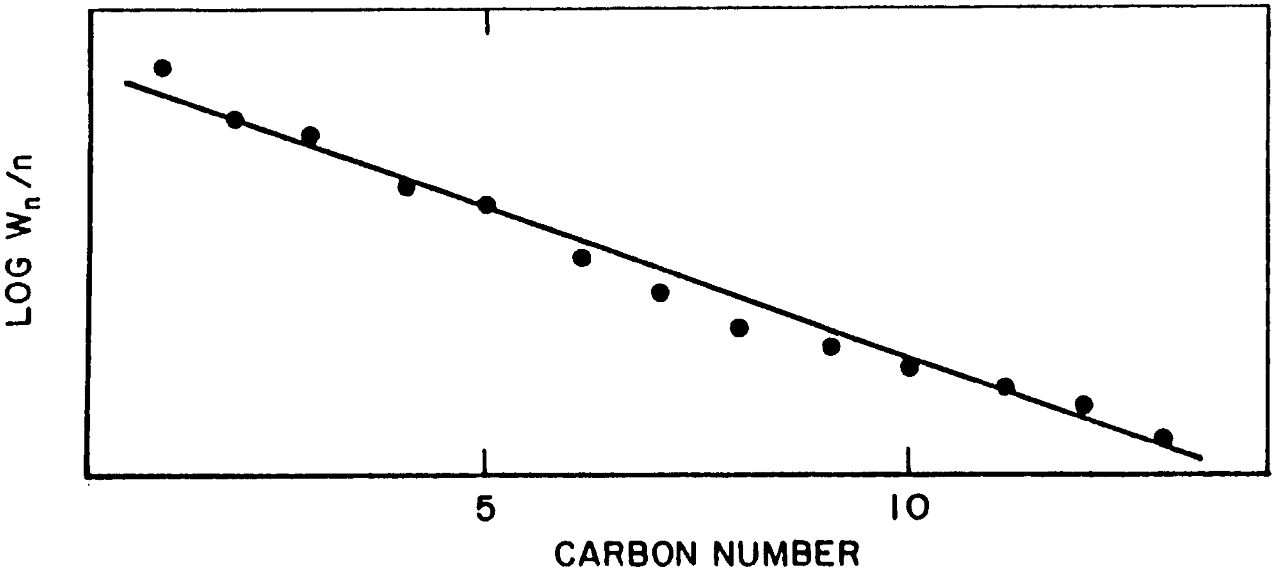

Figure 5-Anderson-Schulz-Flory plot for 120h reaction, Table I.

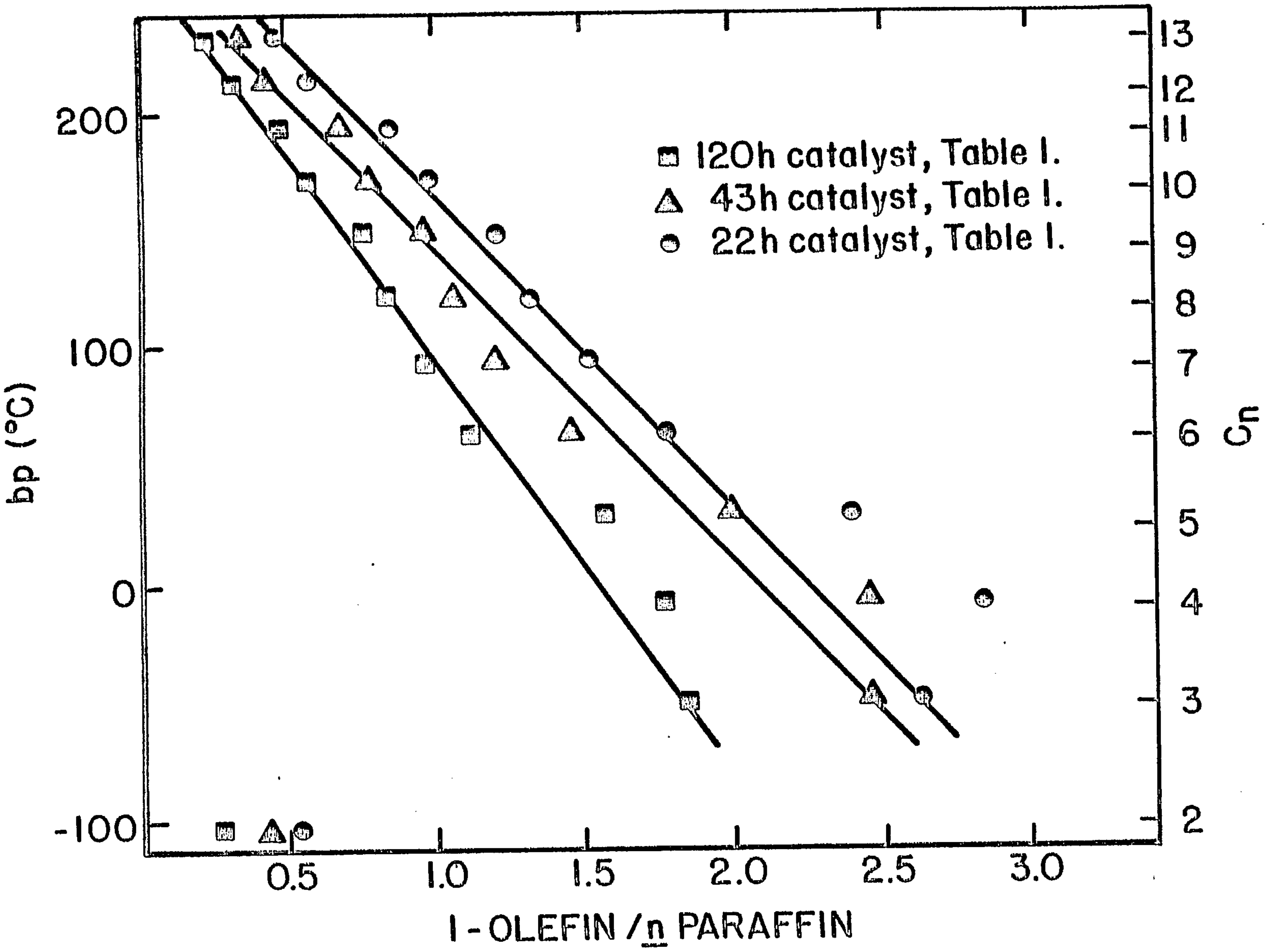

Figure 6 - Comparison of 1-Olefin/n-Paraffin ratios to boiling points of olefins at different catalyst reaction times.

In Figure 7, we have plotted the 1-olefin/n-paraffin ratios vs boiling points under various reaction conditions. Again the C_2 fraction falls far from any relationship held by the other C_n fractions. The C_4 and C_5 fractions appear high in 1-olefin content again, although the C_5 fraction in the reaction conducted at 275°C is not as high as observed in previous examples. The C_3 fraction is more enriched in 1-olefin in this comparison (275°C example) than in previous examples.

It would appear from the examination of Figures 6 and 7 that there may be some relationship between the boiling point of the 1-olefin and the 1-olefin/n-paraffin ratio under a variety of reaction conditions for the C_6-C_{13} hydrocarbons. The C_3-C_5 hydrocarbons show 1-olefin/n-paraffin ratios that approach the linearity established by the C_6-C_{13} fraction but do deviate some from it. The ethylene/ethane ratio does not come close at all to this linearity. This would again seem to indicate the special reactivity of ethylene relative to other 1-olefins in the Fischer-Tropsch reaction. From our analysis to date, we can conclude that the inverse relationship of the C_2 fraction to the rest of the C_n fractions is not due to ethylene cracking, nor thermodynamic parameters, nor steric factors, nor boiling point. We can not rule out an unusually high adsorptivity of ethylene versus the other 1-olefins on the catalyst surface, but we would have difficulty in explaining why such a phenomenon would exist to both the extent and selectivity necessary to explain the observed results.

As mentioned earlier, the trend toward greater n-paraffin content occurs with increasing carbon number. In reactions performed with fresh

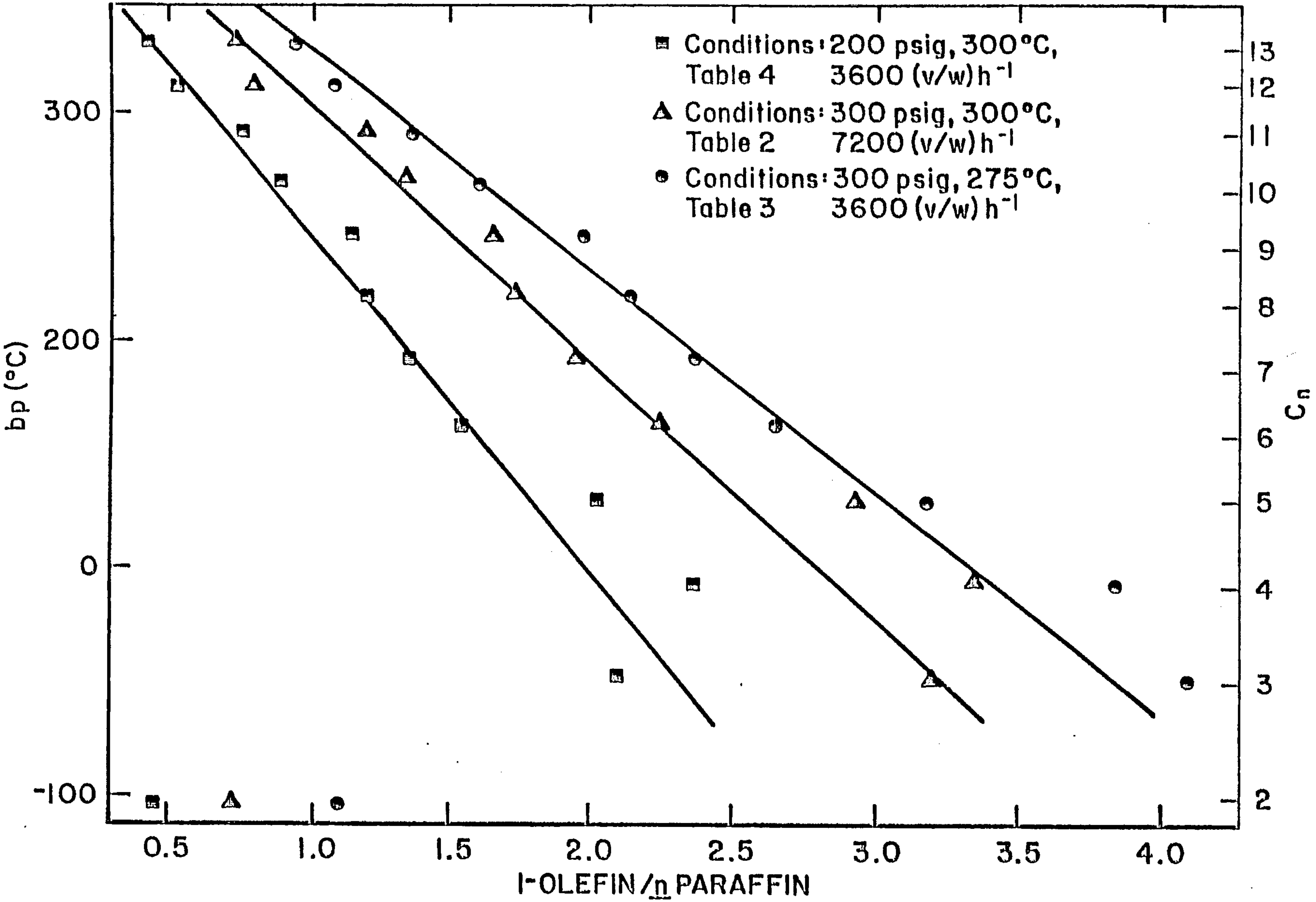

Figure 7 - Comparison of 1-Olefin/n-paraffin ratios to boiling points of olefins under different reaction conditions.

catalyst at 300°C and 300 psig with a space velocity of 3600 (v/w)h^{-1}, one observes a dominance of 1-olefin over n-paraffin from C_3-C_9 with the crossover to more n-paraffin occuring at C_{10}. The crossover with aged catalyst under the same reaction conditions occurred at C_7. Clearly, the age of the catalyst is important, when it can shift the 1-olefin/n-paraffin crossover point by three carbons.

We wanted to examine what effect other parameters might have upon the 1-olefin/n-paraffin ratio. In Table VIII is illustrated the change in the 1-olefin/n-paraffin ratio with respect to space velocity. The temperature and pressure are the same as in Table VII. One would expect an increase in the 1-olefin/n-paraffin ratio with increased space velocity and indeed this was observed. The crossover from 1-olefin to n-paraffin as the major product occurred at C_{12} rather than C_9 when the space velocity was doubled using catalyst which had been on stream for approximately 43 hours.

The effect of lowering the temperature by 25C° is quite dramatic (Table IX). The amount of 1-olefin increased even to the point to where it dominated in the C_2 fraction. The crossover from 1-olefin to n-paraffin as the major product, however, occurred at C_{12} rather than C_9 when the temperature was 25C° higher and for a similar catalyst time on stream. Thus, the lower hydrocarbons experienced significant increases in 1-olefin content but the crossover point was the same as when the space velocity was doubled.

Lower operating pressures led to greater 1-olefin/n-paraffin ratios as expected, but the increase was not nearly as dramatic as was the case with decreased temperature. However, the crossover point was moved three carbons

TABLE VIII. COMPARISON OF 1-OLEFIN/n-PARAFFIN RATIOS AT DIFFERENT SPACE VELOCITIES[a]

Carbon Number	GHSV (v/w)h^{-1}	1-Olefin/n-Paraffin
C_2	3600 7200	0.43 0.73
C_3	3600 7200	2.45 3.19
C_4	3600 7200	2.44 3.33
C_5	3600 7200	1.99 2.92
C_6	3600 7200	1.45 2.24
C_7	3600 7200	1.20 1.95
C_8	3600 7200	1.05 1.72
C_9	3600 7200	0.96 1.65
C_{10}	3600 7200	0.77 1.34
C_{11}	3600 7200	0.67 1.20
C_{12}	3600 7200	0.43 0.80
C_{13}	3600 7200	0.34 0.74

[a] Conditions: 300°C, 300 psig, $H_2/CO = 3:1$, catalyst on stream ca. 45h.

higher to C_{10} versus C_7 for the reaction employing 300 psig and catalyst which was 120 hours on stream (Table X).

The results reported here are from duplicate analysis with little variation between the two. We were concerned, however, about the correlation between different runs made at different times from different catalyst loadings of our reactor tube. A demonstration of this correlation is shown in Table XI. Both run 1 and run 2 were made under identical reaction conditions with only a physical change of the catalyst being made. The results were from catalysts on stream for similar times. The ratios obtained from the two runs were quite similar.

CONCLUSIONS

On-line gas-chromatographic analysis has proved to be a valuable method for studying Fischer-Tropsch reactions under a variety of reaction conditions. The effect upon the reaction due to catalyst age can be readily studied using this method.

Clearly the fate of 1-olefins in the Fischer-Tropsch reaction varies with carbon number. It has been demonstrated that a trend exists, under a variety of reaction conditions, where 1-olefins become formally more hydrogenated with increasing carbon number. The C_2 fraction does not follow this trend and in all instances but one gave a low ethylene/ethane ratio. If the observed increase in _n_-paraffins is due to hydrogenation, then one would have a better chance of incorporating 1-olefins into a growing Fischer-Tropsch chain by adding C_3-C_5 olefins. Adding higher than C_7 hydrocarbons will lead to appreciable hydrogenation of the added 1-olefin and consequently low incorporation. The anomalous behavior of ethylene suggests that it may not be undergoing the same chemistry as other olefins. A detailed study on the fate of ethylene with this catalyst, under the reaction conditions explored, is clearly in order. If ethylene is undergoing appreciable hydrogenation, then it too would be a poor olefin to try to incorporate into a Fischer-Tropsch chain.

The changes in 1-olefin/n-paraffin ratios with changing reaction conditions are about what one would expect although the effect of lowering temperature appears to be the most dramatic. The catalyst age is quite important as it effects not only the 1-olefin/n-paraffin ratio, but the crossover point at which the n-paraffins dominate.

EXPERIMENTAL

REACTOR

The reactor was a plug-flow model mounted in a vertical position above the sampling port of the gas chromatograph. The reactor design is illustrated in Figure 8. The reactor tube was 3/8" stainless steel and was connected, by means of adapters, to a 1/4" stainless steel exit line. The exit line was connected to the sampling valves. The exit line was heated at 300°C during the course of the reaction by heating tape and its temperature was monitored at two points by the means of thermocouple implants. The reaction variables of temperature, flow rate, and pressure were controlled from a control panel.

TABLE IX. COMPARISON OF 1-OLEFIN/n-PARAFFIN RATIOS AT DIFFERENT TEMPERATURES[a]

Carbon Number	Temperature (°C)	1-Olefin/n-Paraffin
C_2	275	1.10
	300	0.43
C_3	275	4.09
	300	2.45
C_4	275	3.84
	300	2.44
C_5	275	3.17
	300	1.99
C_6	275	2.64
	300	1.45
C_7	275	2.37
	300	1.20
C_8	275	2.14
	300	1.05
C_9	275	1.98
	300	0.96
C_{10}	275	1.60
	300	0.77
C_{11}	275	1.36
	300	0.67
C_{12}	275	0.99
	300	0.43
C_{13}	275	0.85
	300	0.34

[a] Conditions: 300 psig, GHSV: 3600 (v/w)h^{-1}, H_2/CO = 3:1, catalyst on stream ca. 45 h.

TABLE X. COMPARISON OF 1-OLEFIN/n-PARAFFIN RATIOS AT DIFFERENT PRESSURES[a]

Carbon Number	Pressure (psig)	1-Olefin/n-Paraffin
C_2	200	0.45
	300	0.27
C_3	200	2.19
	300	1.83
C_4	200	2.36
	300	1.77
C_5	200	2.02
	300	1.56
C_6	200	1.53
	300	1.10
C_7	200	1.35
	300	0.96
C_8	200	1.20
	300	0.82
C_9	200	1.15
	300	0.75
C_{10}	200	0.90
	300	0.57
C_{11}	200	0.77
	300	0.47
C_{12}	200	0.54
	300	0.32
C_{13}	200	0.43
	300	0.22

[a] Conditions: 300 psig, GHSV: 3600 (v/w)h^{-1}, H_2/CO = 3:1, catalyst on stream ca. 45 h.

TABLE XI. CORRELATION BETWEEN DATA OBTAINED FROM RUN TO RUN [a]

Carbon Number	1-Olefin/n-Paraffin Run A	Run B
C_2	0.77	0.79
C_3	2.70	2.59
C_4	3.25	3.13
C_5	3.00	2.71
C_6	2.38	2.28
C_7	2.00	2.05
C_8	1.91	1.91
C_9	1.84	1.85
C_{10}	1.36	1.36
C_{11}	1.16	1.15
C_{12}	0.87	0.93
C_{13}	0.78	0.84

[a] Conditions: 275°c, 100 psig, GHSV: 3600 (v/w)h^{-1}, H_2/CO = 3:1. Run A and Run B are identical with respect to catalyst aging (ca. 100 h on stream) and differ only in that for Run B the reactor tube was replaced with new catalyst and re-aged after obtaining the data for Run A.

MATERIALS

The synthesis gas was 3:1 H_2/CO and was purchased from Scott Specialty Gases. The catalyst used to demonstrate this technique was a CCI fused iron oxide, potassium promoted, catalyst purchased from United Catalysts. It contained 67.1% Fe, 1.82% CaO, 0.17% MgO, 0.21% SiO_2, and 0.60% K_2O.

GAS CHROMATOGRAPH

The gas chromatograph was a Hewlett-Packard 5730A equipped with dual FID and dual TCD capabilities. The columns were operated in the differential mode where the reference columns were identical to the working columns. The stainless steel columns were a 20' x 1/8", 10% SP 2100 on 100/120 Supelcoport for separating hydrocarbons and a 7' x 1/8", 100/120 Carbosieve S column for separating carbon monoxide, carbon dioxide, and the light hydrocarbons. Sample introduction was performed by means of two sample loops of 0.125 ml for the Carbosieve column and 0.250 ml for the SP 2100 column. The sample introduction and sample loop configuration is illustrated in Figure 9. For purposes of illustration, sample valve 1 is shown in the "non-actuated" position and sample valve 2 is shown in the "inject" position. In practice, both valves are actuated at the same time. The data was recorded graphically on a dual-pen strip chart recorder and transferred onto a computer through 2 A/D converters. The flow rates were 30 ml/min for helium (carrier gas), 60 ml/min for hydrogen, and 240 ml/min for air. The injection port and sample loops were heated to 300°C and both detectors were also set at 300°C. The oven was temperature programmed beginning at -50°C with a hold time of 2 min. The oven temperature was then increased at a rate of 8°C/min until 290°C was obtained. The oven was held at 290°C for 32 min. Response factors were determined by standard methods.[3]

METHODS

The CCI catalyst (0.5g) was reduced in a stream of hydrogen with a flow rate of 60 ml/min for 3 h at 450°C and atmospheric pressure and, then, carbided with a flow of carbon monoxide at 60 ml/min at 250°C for 1 h at atmospheric pressure. The Fischer-Tropsch reaction was run using a variety of temperature and pressures (see text) but most commonly was effected at 300°C and 300 psig using a 3:1 synthesis gas (H_2/CO) mixture at a flow rate of 30 ml/min.

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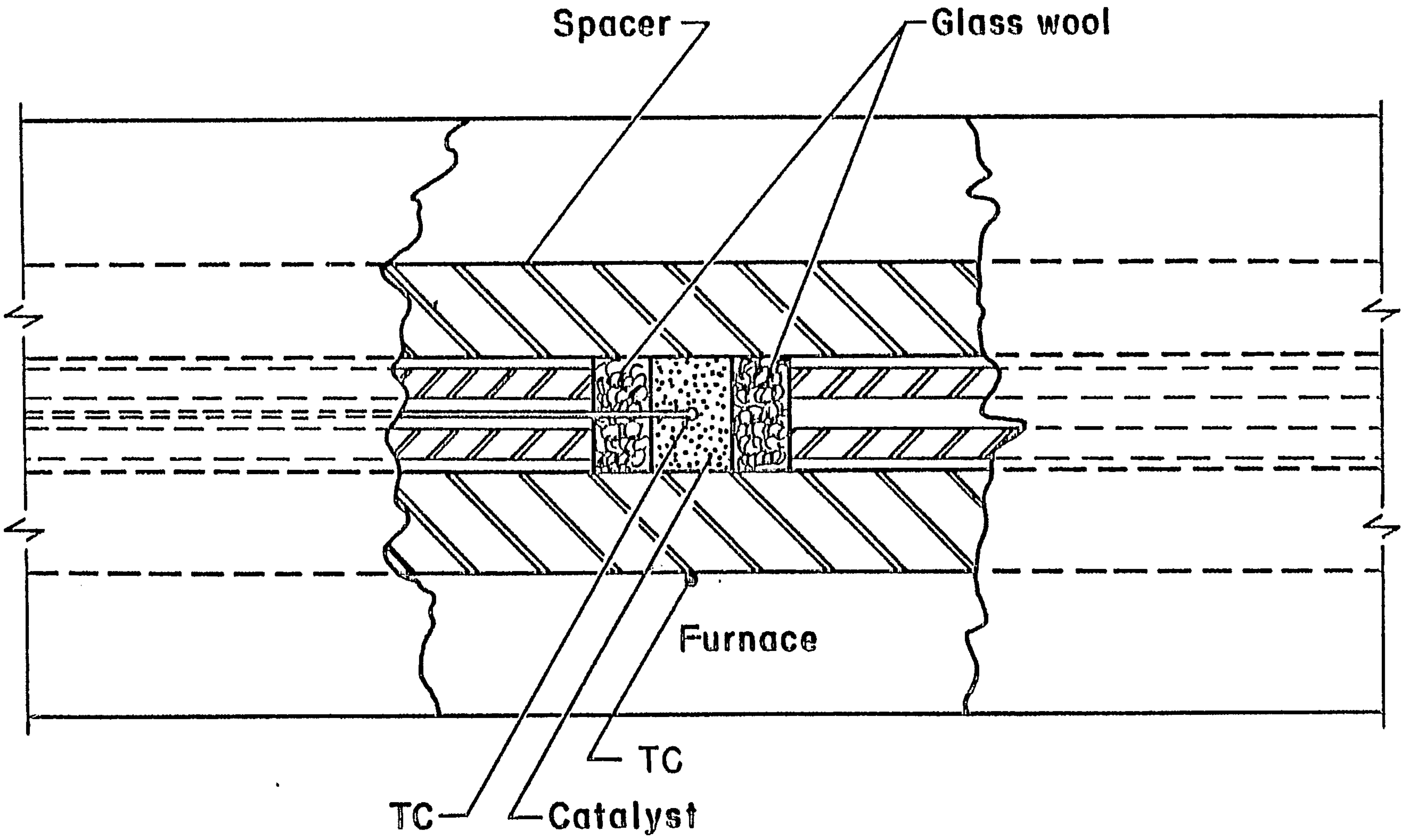

Figure 8.- Reactor

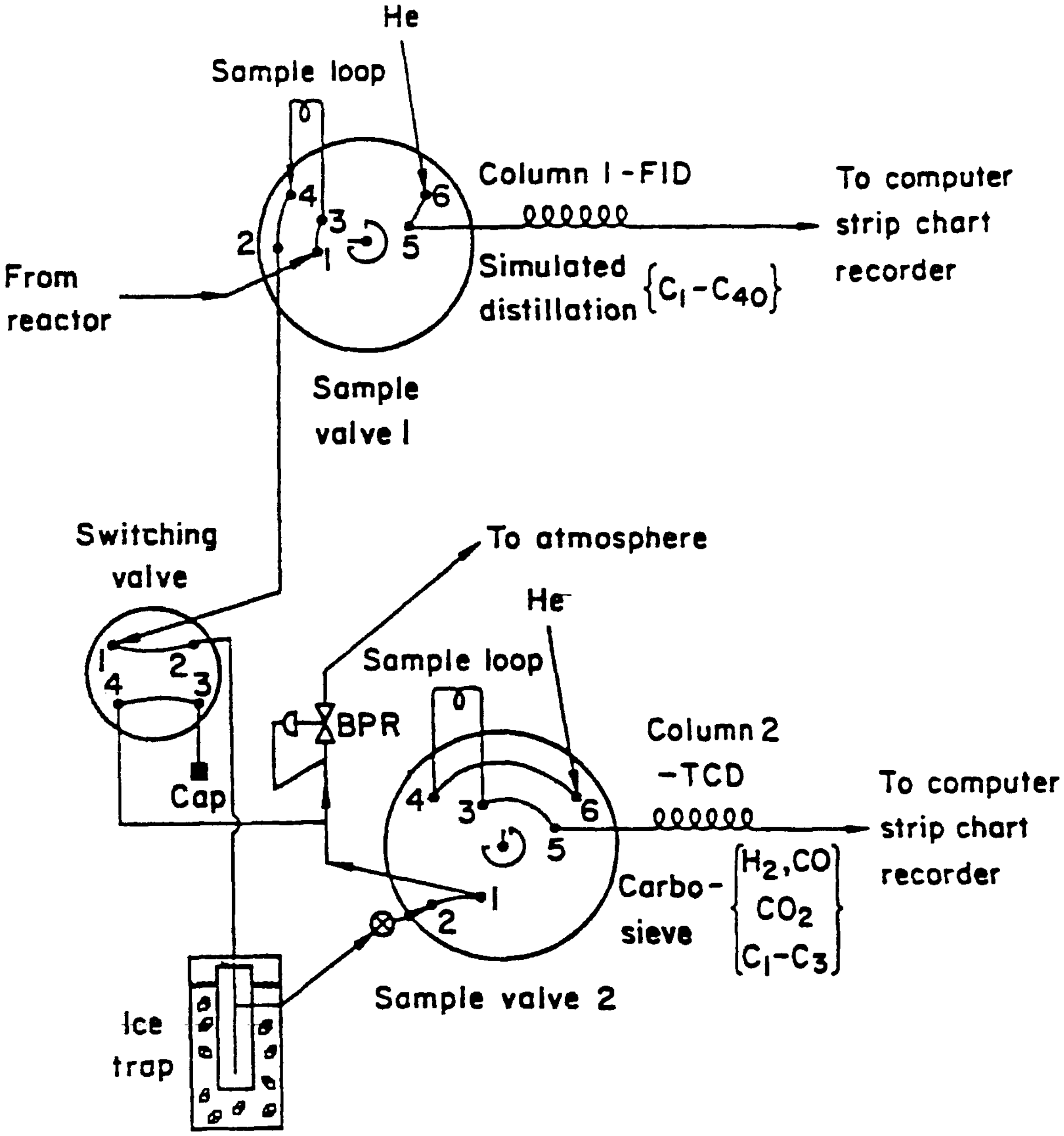

Figure 9 - Sample valve compartment.

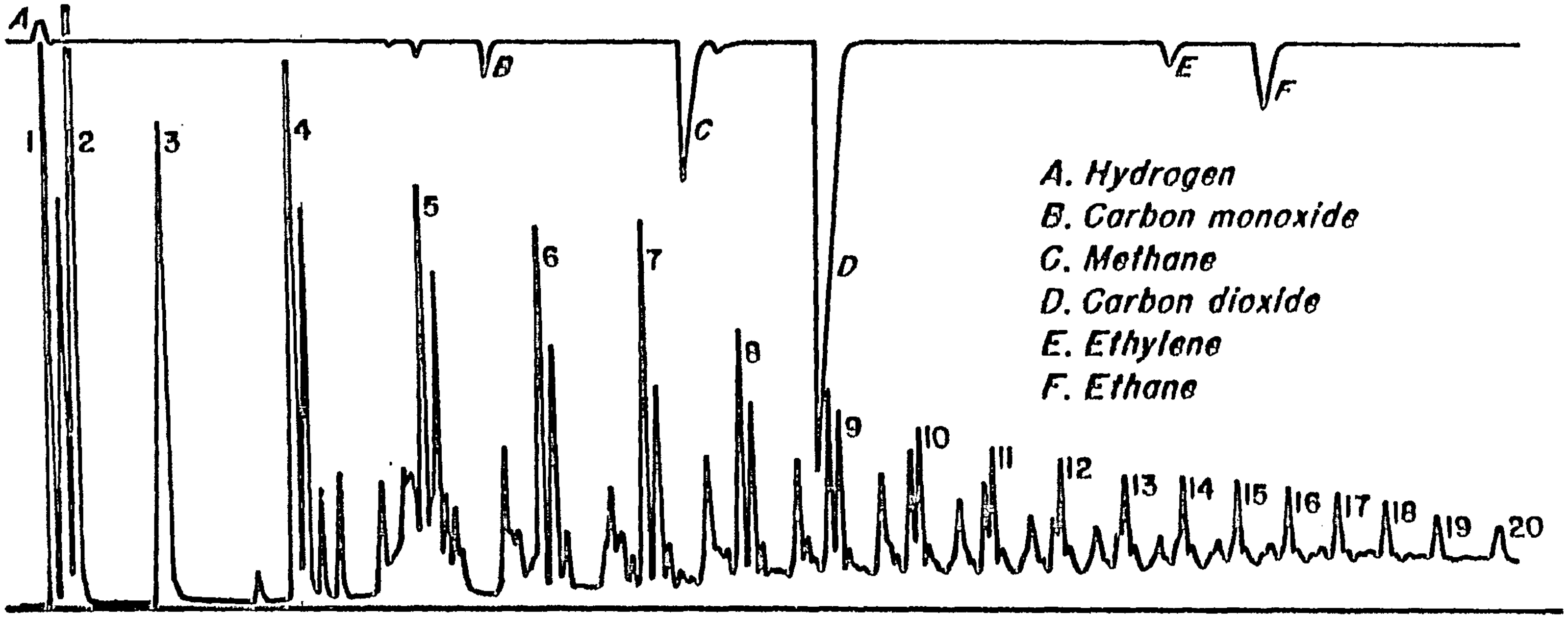

Figure 10- Gas chromatogram of Fischer - Tropsch Product. Peaks numbered 1-20 represent C_1-C_{20} hydrocarbons as detected by FID. Peaks labeled *A*-*F* were detected on the TCD.

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3. For a discussion on determining and using response factors see: H.M. McNair and E.J. Bonelli, Basic Gas Chromatography, 5th edition, Varian, Palo Alto, 1969.

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