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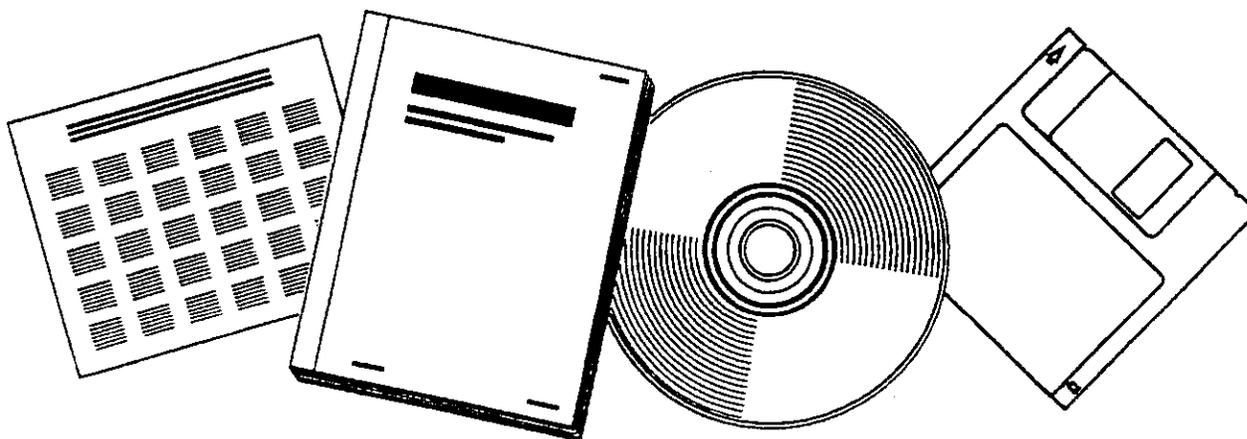
FISCHER-TROPSCH SYNTHESIS IN SLURRY-REACTOR SYSTEMS. QUARTERLY REPORT, MAY 1, 1982-JULY 31, 1982

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Fischer-Tropsch Synthesis in Slurry-Reactor Systems

Quarterly Report for Period

May 1, 1982 to July 31, 1982

MASTER

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and

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I. SUMMARY

In the quarterly report for the period ending July 31, 1981 we listed four papers that were being submitted for publication. All four have now been published and we list them here for reference:

C.N. Satterfield, G.A. Huff, Jr., and H. Stenger, "Effect of Carbon Formation on Liquid Viscosity and Performance of Fischer-Tropsch Bubble-Column Reactors," Ind. Eng. Chem., Process Des. Develop., 20, 666-670 (1981).

C.N. Satterfield and G.A. Huff, Jr., "Usefulness of a Slurry-Type Fischer-Tropsch Reactor for Processing Synthesis Gas of Low Hydrogen-Carbon Monoxide Ratios," Can. J. Chem. Eng., 60, 159-162 (1982).

C.N. Satterfield and G.A. Huff, Jr., "Carbon Number Distribution of Fischer-Tropsch Products Formed on an Iron Catalyst in a Slurry Reactor," J. Catalysis, 73, 187-197 (1982).

C.N. Satterfield, G.A. Huff, Jr., and J.P. Longwell, "Product Distribution from Iron Catalysts in Fischer-Tropsch Slurry Reactors," Ind. Eng. Chem., Process Design Develop., 21, 465-470, 1982.

Our paper entitled, "A Stirred Autoclave Apparatus for Study of the Fischer-Tropsch Synthesis in a Slurry Bed. I. Reactor and Trapping Procedures," a copy of which was appended to the August-October, 1981 quarterly report, is now in press in Ind. Eng. Chem., Fundamentals.

During June, Professor Satterfield presented invited lectures on recent M.I.T. work on Fischer-Tropsch synthesis, at the British Petroleum laboratories in London and at the Engler-Bunte Institute, University of Karlsruhe, West Germany. He also participated in the Symposium on

"Catalytic Reactions of One Carbon Molecules" held in Bruges, Belgium in June.

We have previously reported that our studies with addition of olefin to synthesis gas on an iron catlayst showed no evidence of incorporation of ethylene into the growing chains, contrary to a report by Dwyer and Somorjai. Some additional runs were made and the whole subject has been reviewed and interpreted. A copy of a manuscript describing this work is attached. It will be submitted shortly to J. Catalysis.

A summary of the doctoral thesis of George A. Huff, Jr., which covers most of our work on reduced fused magnetite to date, was prepared and a copy is attached.

Particularly interesting was the finding that the total product distribution on a carbon number basis clearly followed a double α value. From C_1 to C_{10} an α of about 0.70 was typical, but above C_{20} α was about 0.93. This means that the % conversion of synthesis gas to liquid fuels would be significantly greater than predicted from the usual single α plot based on light gas analysis. The results are interpreted in terms of a 2-site mechanism. Similar observations were reported in Germany during World War II, in the Schwarzheide test on iron catalysts, but subsequently there was considerable questioning as to whether the effect was real. The present findings clearly support the German observations.

OLEFIN INCORPORATION IN THE
FISCHER-TROPSCH SYNTHESIS ON AN IRON CATALYST

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ABSTRACT

Addition of ethylene or 1-butene to synthesis gas caused no change in
the molecular weight distribution of products, α. Material balances showed
the possibility of a slight degree of incorporation of ethylene into growing
chains. Some ethylene was hydrogenated to ethane but no hydrogenation of
1-butene occurred. Studies were with a reduced alkalized fused iron
catalyst in a well stirred slurry reactor, at 248°C and 790 or 1480 kPa
total pressure.

The extent to which olefins may be incorporated into growing chains
during Fischer-Tropsch synthesis is of mechanistic significance and also
of practical importance since it is a possible means of altering the
molecular weight distribution of the products or increasing the forma-
tion of higher molecular weight hydrocarbons. At the usual synthesis
temperatures the incorporation of, e.g. ethylene or 1-butene into
synthesis products is highly favorable thermodynamically although
that for 1-butene is somewhat less favorable than for ethylene (1).

Two early studies with C-labelled ethylene or propylene (2,3)
indicated that on iron catalysts only a few percent of the added olefins
were incorporated into higher hydrocarbons but in a more recent study (4)
it was reported that the addition of ethylene or propylene markedly
shifted the selectivity to heavier products. The present studies were

designed to help resolve this disagreement.

Hall et al. (2) passed synthesis gas of H_2/CO ratio equal to 1 and containing 1 to 1.25 mole % radioactive ethylene over either of two reduced fused iron catalysts in a fixed bed reactor at 224°C. With an iron catalyst promoted with 0.6% SiO_2, 0.6% Cr_2O_3, 4.6% MgO and 0.6% K_2O at 790 kPa, about 6 mole % of the ethylene was incorporated into higher hydrocarbons. With an iron catalyst promoted with 0.64% Al_2O_3 and 2.0% ZrO_2 but containing no potassium at 100 kPa, about 12% of the ethylene was incorporated into higher hydrocarbons. In both experiments most of the labelled ethylene was hydrogenated to ethane.

Schulz et al. (3) investigated the effect of ^{14}C-labelled ethylene or propylene over an alkalized iron catalyst in a fixed-bed reactor at 2.1 MPa and 220°C. They added 0.2 to 0.3 mole% olefin to synthesis gas with a H_2/CO molar ratio of 2.0. About 9% of the ^{14}C-labelled ethylene but only 1% of the propylene was converted to higher hydrocarbons. In both cases, the major portion of the tagged olefins was hydrogenated to the saturated paraffins.

In a more recent study, Dwyer and Somorjai (4) reported that the addition of 0.04 to 2.7 mole% ethylene or propylene to synthesis gas with a H_2/CO molar ratio of 3 noticeably shifted the selectivity to heavier products. Experiments were conducted with an initially evacuated, unalkalized iron foil at 610 kPa and 300°C in an isolation cell over a catalyst lifetime of 2 to 3 hr. Loss of Fischer-Tropsch activity was attributed to excessive carbon deposition on the catalytic surface. Total conversion of CO was <1% in their runs. In a representative experiment, after 90 min of reaction most of the ethylene had been converted to ethane but 8 mole % of the original ethylene at 2.7 mole% concentration had been converted to higher

hydrocarbons. A chain growth probability factor α of 0.56 was calculated, based on a Schulz-Flory distribution for C_1 and C_3 to C_5 hydrocarbons. A much lower value of $\alpha = 0.30$ was observed when only 0.04 mole% ethylene was added. When propylene was added, a value of $\alpha = 0.70$ was reported. Dwyer and Somorjai reasoned that the increase in α with increasing ethylene partial pressure, indicative of a higher average molecular-weight product, indicated that ethylene participated directly in the propagation step. Their results suggested that incorporation of alpha-olefins into growing chains on the catalyst surface was a major reaction pathway for producing higher molecular-weight products.

EXPERIMENTAL

The apparatus and analytical procedures used in this study are described in detailed elsewhere (5,6). Synthesis gas either with or without added ethylene or 1-butene was passed continuously into a 1-liter, mechanically-stirred autoclave about half-filled with an essentially nonvolatile and inert liquid, normal-octacosane of > 99% purity, in which the catalyst was suspended. The contents were well mixed so the reactor behaved as a C.S.T.R. Volatile products were removed overhead continuously while the catalyst and inert liquid remained in the reactor for the duration of a run. After an initial period, steady-state operation with regard to catalytic activity and selectivity was obtained over the entire run.

The catalyst (from United Catalysts, Inc., and designated C-73) was a fused iron containing 2.0-3.0% Al_2O_3, 0.5-0.8% K_2O, 0.1-1.2% CaO, and < 0.4% SiO_2, on an unreduced basis. About 75 g of crushed catalyst was prereduced in a separate vessel with hydrogen at a space velocity of 10,000 hr^{-1}, 400°C, and atmospheric pressure. It was then slurried

with the octacosane to produce a 15 wt% suspension (unreduced basis).

Premixed gases from cylinders were employed. The synthesis gas composition was about 55 mole% hydrogen and 45 mole% carbon monoxide. To this was added 1.5 mole% ethylene or 0.86 mole% 1-butene. The gas was fed to the reactor at a space velocity of approximately 6.5 L gas (at S_{TP})/min-kg catalyst (unreduced basis). Reactor temperature was 248°C, and total pressure was either 790 or 1480 kPa. At these reaction conditions, carbon monoxide conversions greater than 90% were obtained. These were sought since significant readsorption of olefins would seem to be most likely when competition with carbon monoxide, which is strongly bound onto the catalyst, is minimized.

A run was also conducted in which synthesis gas with added ethylene was fed to the reactor filled with octacosane, but without catalyst. No secondary hydrogenation was observed which established that the stainless-steel reactor walls were effectively inert and that homogneeous reaction was negligible.

The products were analyzed by gas chromatography. They were characterized by carbon number on a total organic basis, which included hydrocarbons plus oxygenates.

RESULTS

We will show that our products follow the same Flory distribution in the presence of added ethylene and 1-butene as they do in the absence of added olefin. For this to be true, alpha-olefins must either be incorporated with the same chain propagation rate as for addition of single carbon units or not be significantly incorporated into growing chains. A significant fraction of the ethylene was hydrogenated to ethane but the 1-butene remained unreacted.

The Fischer-Tropsch products over an iron catalyst, including C_1 and C_2 species have been shown to follow closely a Flory distribution (6), which is derived assuming that single carbon units are added one at a time onto the terminus of a growing linear chain. The mole fraction m_n of molecules in the product mixture of carbon number $\underline{n}$ is given by:

$$m_n = (1 - \alpha)\alpha^{n-1}, \tag{1}$$

where α is the probability of chain growth and is taken to be independent of molecular size. The term m_n in this expression is based on the total moles of organic product synthesized, and here does not include the moles of ethylene or 1-butene added to the feed.

Considering studies with ethylene addition, it is difficult to determine with high accuracy the quantity of C_2 compounds that would be expected to exist in the exit stream in the absence of ethylene incorporation for comparison with experimental results, in part because a considerable part of the C_2 product is ethanol. Therefore we considered only the C_3 to C_8 fraction of the product for analysis of results. Equation (1) then becomes:

$$m_n' = (M_T/M_{3-8})(1 - \alpha)\alpha^{n-1}, \tag{2}$$

where m_n' is the mole fraction of carbon number n (where $3 \leq n \leq 8$), within the C_3 to C_8 portion, M_{3-8} is the moles of C_3 to C_8 organic, and M_T is the total moles of organic produced by the synthesis.

Data are more conveniently represented by the logarithmic form of Eq. (2):

$$\ln(m_n') = \lg[\frac{M_T(1 - \alpha)}{M_{3-8}\,\alpha}] + n \ln(\alpha). \tag{3}$$

A plot of $\ln(m_n')$ as a function of n yields the value of α from the slope. The value of α cannot be calculated from the ordinate

intercept as M_T is not generally known. However, with the value of α calculated from the slope, the ratio of M_{3-8}/M_T backcalculated from the intercept must be less than one for internal consistency.

Runs with and without added olefin were conducted at various times-on-stream with each of two batches of catalyst to establish reproducibility and to verify steady-state behavior. Table 1 gives the % conversion of H_2 and of CO (note that some CO disappears and H_2 is formed by the water gas shift reaction) and the ethylene and butylene partial pressures in the exit gas. The H_2/CO molar feed ratio was 1.27 for Runs 1-1 and 1-2, and was 1.20 for Runs 1-3, 1-4 and 2-1 to 2-4 . The product distribution by carbon number for each of the four data sets without added olefin (Runs 1-1, 1-4, 2-1 and 2-2) is plotted in Fig. 1 according to the modified Flory relationship given by Eq. (3). There was no trend with time on stream, catalyst batch, carbon monoxide conversion or partial pressure of ethylene or butene, which in this case were all formed by the synthesis.

From the line in the figure, an α of 0.59 was calculated from the slope by Eq. (3) [as $\ln(\alpha)$]. The term M_{3-8}/M_T, estimated from the ordinate intercept [as $M_T(1 - \alpha)\alpha^2/M_{3-8}$ at n = 3], equaled 0.34. As expected, the value was less than one. For these same data, the experimental ratio for the four runs was calculated to be 0.40, which is good agreement. '

Figure 2 shows data for Runs 1-3, 2-3 and 2-4 in which 1.5 mole% ethylene was added to the synthesis gas. The chain growth probability was 0.59, the same value as for runs without added ethylene; i.e., adding ethylene did not alter the product distribution.

Table 2 compares matched pairs of runs with and without added ethylene (e.g. 2-2 with 2-4, 1-4 with 1-3 and 2-1 with 2-3). From 18 to 32% of the added ethylene became hydrogenated to ethane, more at the higher pressure. Dry (7) also observed that ethylene appreciably reacted with hydrogen when it was added to the feed gas over an iron catalyst at 335°C. He reported that C_{3+} olefins were not hydrogenated under similar conditions. Comparison of matched pairs shows no significant effect of ethylene addition on olefin-paraffin ratio of, e.g., the C_4 or C_6 product.

For each run with added ethylene a material balance on the C_2 fraction could be made by comparison with a matched run without added ethylene. In such a comparison adjustment must be made for slightly different flow rates and slightly different catalyst activities between the pair of runs.

The amount of C_2 products expected if no added ethylene were incorporated into growing chains was calculated with adjustment from the base run using the amounts of C_3 products formed in each of the two runs. This adjustment on average was ±8%. By this procedure it was calculated that a slight amount of ethylene disappeared beyond conversion to ethane. The disappearance averaged about 5% and was the greatest at high % CO conversions.

The C_3 to C_8 carbon number distribution is depicted in Fig. 3 for run 1-3 in which 0.86 mole% 1-butene was added to the feed. Unlike the case with ethylene, less than 0.5% of the 1-butene was hydrogenated to n-butane under the synthesis conditions. Hence, the C_4 produced by synthesis could be readily calculated by subtracting the 1-butene added to the feed from the total C_4 in the exit stream. This permitted Fig. 3 to be constructed on the same

C_3 to C_8 basis as Figures 1 and 2 for simpler comparison of the results.
The product distribution was similar to those obtained with pure synthesis
gas (Fig. 1) and the same probability of chain growth $\alpha = 0.59$ was
calculated.

DISCUSSION

A slight degree of incorporation of an olefin into the product
might be difficult to identify as a perturbation from a straight line
on a semi-logarithmic plot, but we can find no evidence for this
by calculation of α values. Material balances indicate that it may
occur to the extent of 5 to 10%.

This finding agrees with studies conducted at SASOL (7) in which
a fluidized-bed reactor was operated at 335°C with an iron catalyst.
An olefin-rich oil cut in the gasoline boiling range was extensively
recycled to the reactor (2 volumes oil recycled/volume oil produced).
There was no indication that the oil had been chemically altered even
with 93% synthesis gas conversion; incorporation of the light oil did
not occur.

Studies by Feimer et al. (8) also support this conclusion. They
studied a precipitated, copper-potassium promoted, iron catalyst
operating at steady state in a fixed-bed reactor. The C_1 to C_5
hydrocarbon product distribution, measured at five points along the
bed, was independent of reactor length, and hence ethylene partial
pressure, at 233°C, 1490 kPa, and H_2/CO molar feed ratio of 2.3 and
CO conversion up to 67%. This observation implies that olefin
incorporation was negligible. At very high CO conversions the
reactor profile for ethylene and ethane suggested that ethylene
hydrogenation and/or incorporation into product might be more
important under these conditions.

The different results of Dwyer and Somorjai (4) might be related
to the absence of alkali in the catalyst they used. In pulsing type
studies with a Ru catalyst Nijs and Jacobs (9) reported that incorpora-
tion of alpha-olefins into growing organic chains was significantly
higher on an acidic support than on a neutral support, and the results
of Hall et al. (2) could be interpreted as primarily an effect of
potassium content causing lesser ethylene incorporation into products.

Alternately, and more probably, Dwyer and Somorjai's results can
be attributed to the fact that their catalyst had not reached steady-
state activity and was probably an incompletely carburized, polycrystal-
line iron. Krebs et al. (8) showed with a reduced magnetite catalyst
that the product distribution and value of α changed markedly during
the first few hours on stream, and Raupp and Delgass (11) and Amelse
et al. (12) related major changes in catalyst properties over the first
few hours to surface reconstruction and iron carbide formation.

Some have contended that the typically low value for C_2 on a
Schulz-Flory plot of hydrocarbon products resulted from significant
ethylene incorporation, and hence, loss of ethylene into growing chains
on the iron surface. However, Satterfield and Huff (6) demonstrated
that a low value at C_2 was caused by neglecting oxygenates. On a
total organic basis, a Flory plot of the products from C_1 to about
C_{20} was completely linear for an alkalized iron catalyst at steady
state.

ACKNOWLEDGMENT

REFERENCES

1. Anderson, R.B., in Catalysis, Vol. 4 (P.H. Emmett, ed.), Reinhold, New York, 1956, p. 15.

2. Hall, W.K., Kokes, R.J., and Emmett, P.H., J. Am. Chem. Soc., 82, 1027 (1960).

3. Schulz, H., Rao, B.R., and Elstner, "., Erdoel Kohle Erdgas Petrochem. Brennst. Chem. 23, 651 (1970).

4. Dwyer, D.J., and Somorjai, G.A., J. Catal. 56, 249 (1979).

5. Huff, G.A., Jr., and Satterfield, C.N., Ind. Eng. Chem. Fundam., in press.

6. Satterfield, C.N., and Huff, G.A., Jr., J. Catal. 73, 187 (1982).

7. Dry, M.E., in Catalysis - Science and Technology, Vol 1 (J.R. Anderson and M. Boudart, eds.), Springer-Verlag, Berlin, 1981. - What pp.?

8. Feimer, J.L., Silveston, P.L., and Hudgins, R.R., I&EC Prod. Res. Dev. 20, 609 (1981).

9. Nijs, H.H., and Jacobs, P.A., J. Catal. 66, 401 (1980).

10. Krebs, H.J., Bonzel, H.P., and Schwarting, W., J. Catal. 72, 199 (1981).

11. Raupp, G.B., and Delgass, W.N., J. Catal. 58, 361 (1979).

12. Amelse, J.A., Schwartz, L.H., and Butt, J.B., J. Catal. 72, 95 (1981).
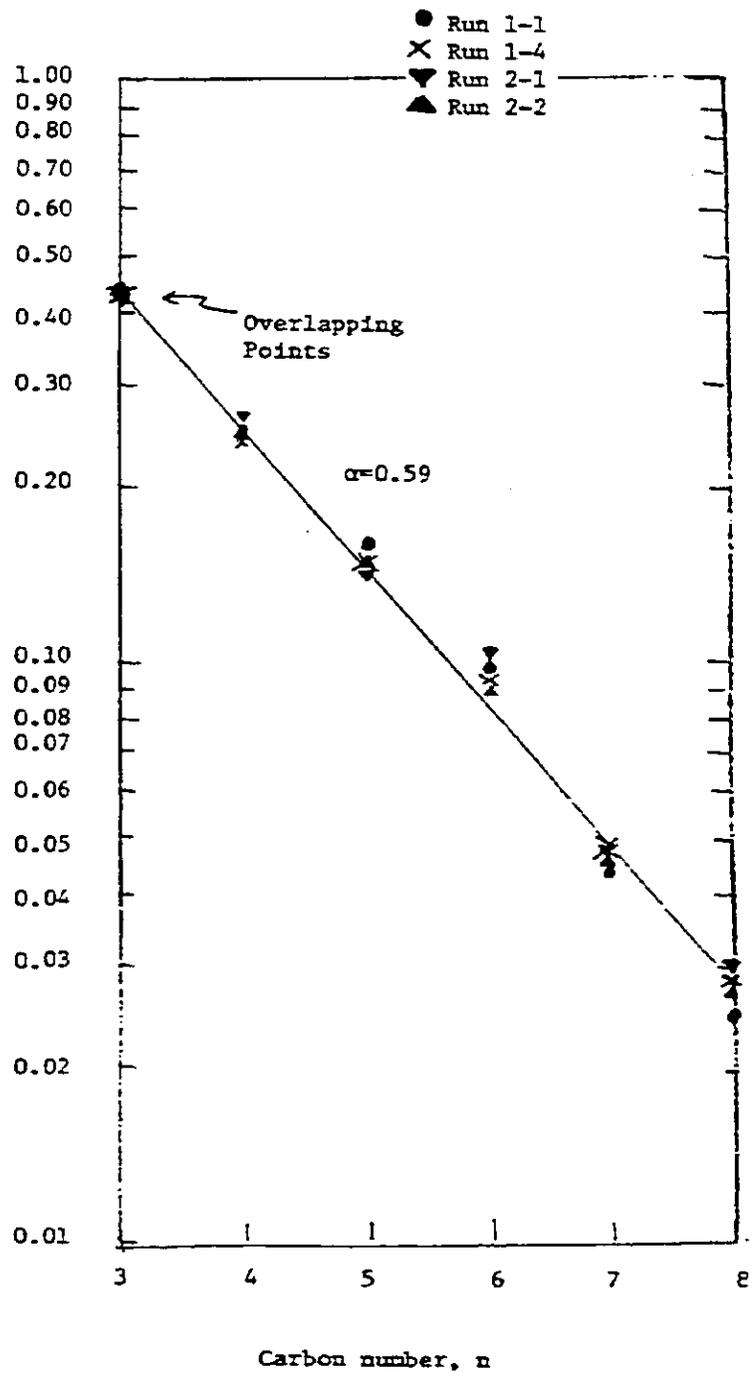
Figure 1. Flory Distribution.
Synthesis Gas Alone.
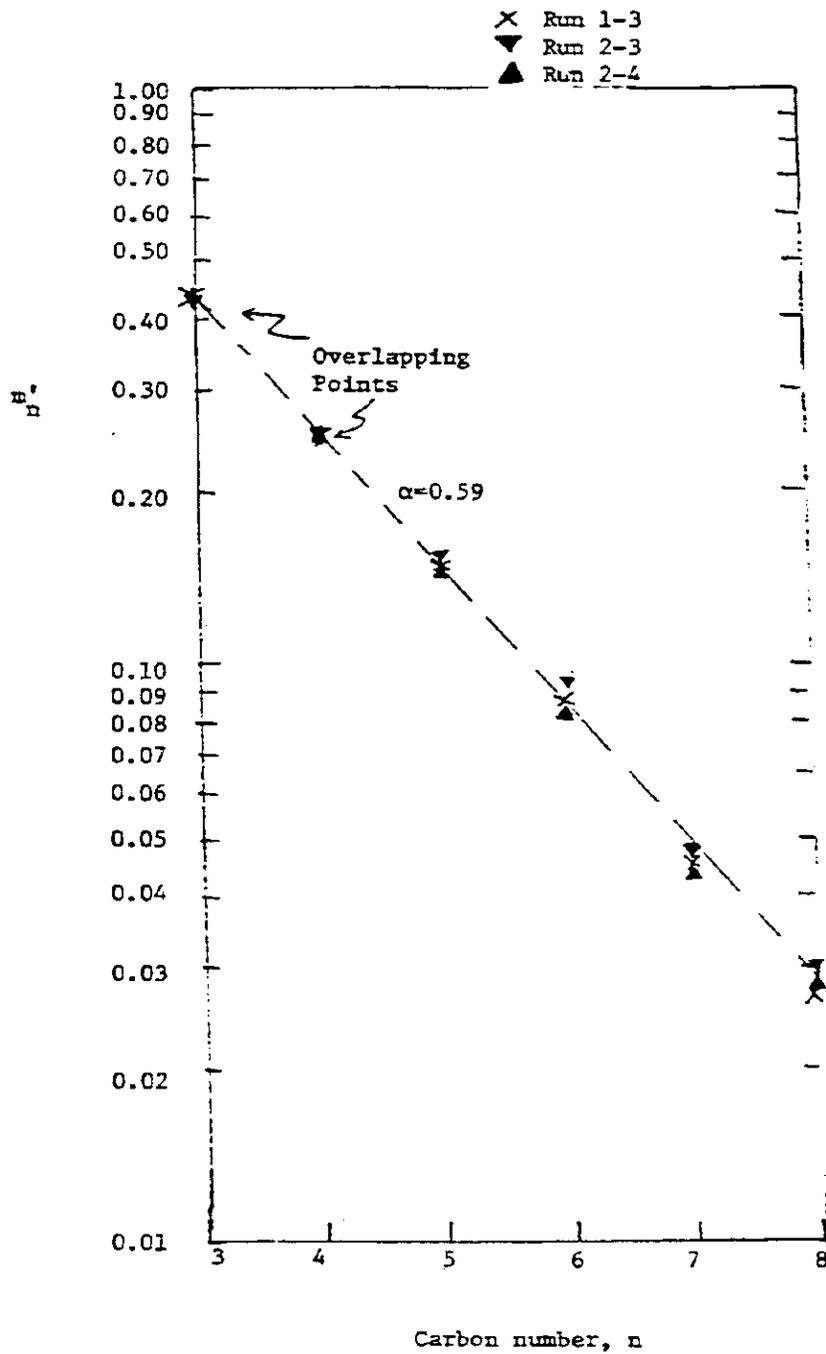
Figure 2. Flory Distribution.
1.5 mole% Ethylene Added to the
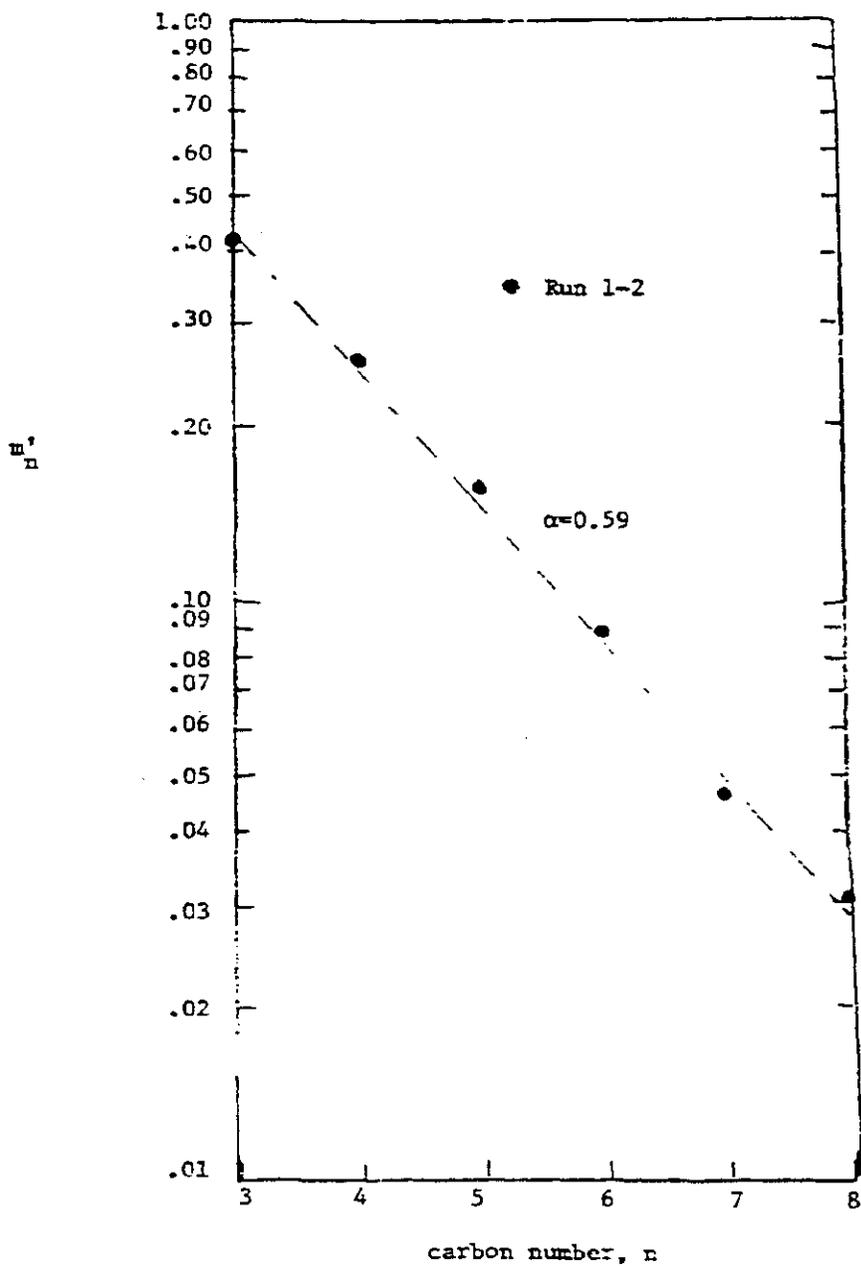Synthesis Gas

Figure 3.   Flory Distribution
            0.86 mole% 1-butene added to
            the synthesis gas.

Table 1. Summary of Experimental Results

Run No.	Time on Stream (hr)	Exit $P_{C_2H_4}$ (kPa)	Exit $P_{C_4H_8}$ (kPa)	P_{total} (kPa)	% Conversion H_2	% Conversion CO
Catalyst Batch 1						
1-1	220	21.8	15.2	1480	57	97
1-2[a]	290	21.6	41.2	1480	60	97
1-3[b]	625	25.1	6.4	790	49	93
1-4	675	9.9	6.1	790	51	93
Catalyst Batch 2						
2-1	120	10.0	6.1	790	48	90
2-2	150	19.9	14.7	1480	57	96
2-3[b]	170	24.2	5.6	790	48	89
2-4[b]	210	43.9	13.5	1480	56	95

[a] 0.86 mole % 1-butene added to feed.

[b] 1.5 mole % ethylene added to feed.

Table 2. Effect of Added Ethylene on
Molar Ratio of Alpha-Olefin/Normal Paraffin

Run No.	C_2[a]	C_4	C_6	Mole % of Added C_2H_4 Hydrogenated	P_{total} (kPa)
Pure Synthesis Gas					
2-2	1.4	4.7	3.9	-	1480
1-4	1.9	4.9	3.9	-	790
2-1	1.8	5.2	4.2	-	790
Synthesis Gas + 1.5 mole % C_2H_4					
2-4	0.1	4.6	3.4	32	1480
1-3	0.5	5.0	4.0	22	790
2-3	0.5	5.5	4.3	18	790

[a] $\dfrac{\text{moles } C_2H_4 \text{ in effluent/min} - \text{moles } C_2H_4 \text{ in feed/min}}{\text{moles } C_2H_6 \text{ in effluent/min}}$