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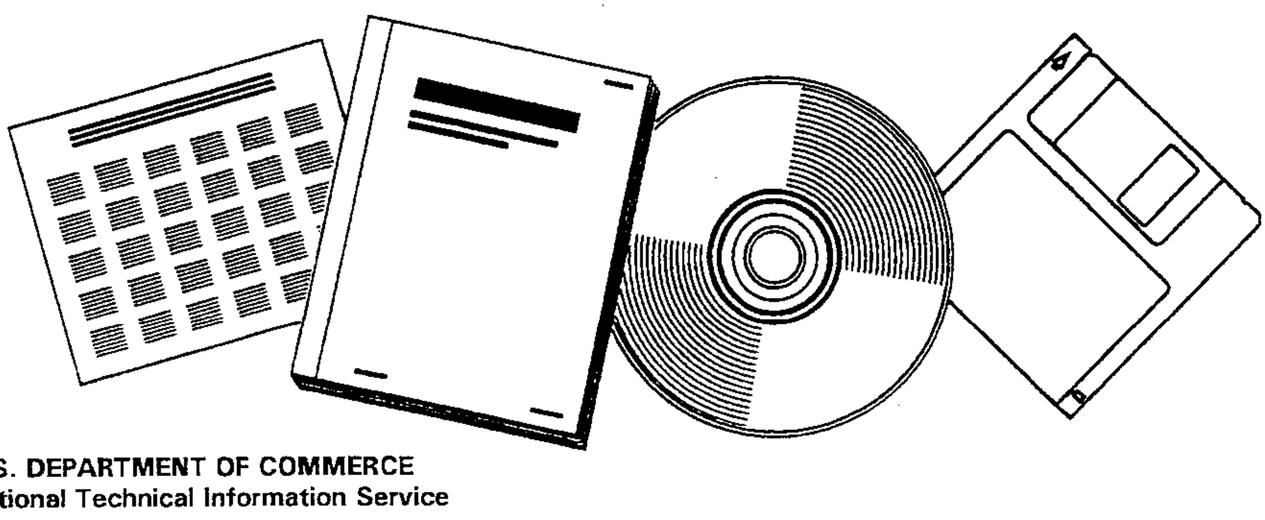
FISCHER-TROPSCH SYNTHESIS IN SLURRY-REACTOR SYSTEMS. QUARTERLY REPORT, FEBRUARY 1, 1982-APRIL 30, 1982

Co Catalyst

MASSACHUSETTS INST. OF TECH., CAMBRIDGE.
ENERGY LAB

1982



U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

Fischer-Tropsch Synthesis in Slurry-Reactor Systems

Quarterly Report for Period

February 1, 1982 to April 30, 1982

Department of Chemical Engineering

and

Energy Laboratory

Massachusetts Institute of Technology

Cambridge, Massachusetts

Report No.: DOE/PC40771-4

Grant No.: DE-FE22-81PC40771

Submitted by:

C.N. Satterfield

T. Bartos

G.A. Huff, Jr.

H. Stenger

DOE/PC/40771--4

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I. SUMMARY

A detailed report on our analytical methods has now been prepared entitled "A Stirred Autoclave Apparatus for Study of the Fischer-Tropsch Synthesis in a Slurry-Bed II. Analytical Procedures," by George A. Huff, Jr., Charles N. Satterfield, and Martin H. Wolf. A copy is appended. Cycled Separately

Studies with the fused iron catalyst at 285°C showed noticeable deactivation over a four-hour period, with a value of $\alpha = 0.66$ based on light-gas analysis. This compares with values of 0.67 to 0.73 found over the same catalyst at 263°C to 232°C.

Scouting studies with an unpromoted Co/kieselguhr catalyst showed a 23% loss of activity over the course of the run. Values of α are much more sensitive to degree of conversion on this catalyst than that found with iron.

Studies in which ethylene or 1-butene was added to synthesis gas showed no effect on α over the fused iron catalyst, contrary to the results reported by Dwyer and Somorjai.

II. DETAILED RESULTS

A. Fused Iron Catalyst at Elevated Temperature

A single run was conducted with the fused iron catalyst (United Catalyst, Inc: #C71) at 285°C to compare with our earlier studies at 232, 248 and 263°C. Table 1 lists the operating conditions. At 285°C the catalyst deactivated noticeably over a 4 hour period preventing a material balance from being obtained at steady state. However a Flory plot of the light gas components remained approximately constant over the period. Products of carbon numbers greater than 5 are significantly condensed in the liquid traps, so they could not be determined quantitatively from the light gas analysis. The Flory plot of the C1 to C5 components resulted in an alpha of 0.66 (Figure 1), which is consistent with values ranging from 0.67 to 0.73 previously obtained between 263°C and 232°C, over a wide range of operating conditions.

Cobalt Catalyst

A scouting run was performed with a reduced unpromoted cobalt on kieselguhr catalyst from United Catalyst, Inc. (#G61). Table 2 summarizes the results of the 20 material balances (MB's) completed during the run. A detailed analysis of the kinetics was not attempted since it is uncertain whether the catalyst was at a constant activity during the run. Comparing the conversion levels of MB1 and MB14 (identical conditions) a loss in activity of 23% occurred.

A second difficulty was the imprudent variation of total pressure between consecutive MB's to achieve different levels of conversion. Rapidly changing the total reactor pressure causes an unsteady state boiling off or accumulation of the products above about C9. Thus the overhead product that was reflective of the catalyst selectivity was the C1 to C8 fraction.

Figure 2 is a typical Flory plot based on MB1. The dip at C2 and the high C1 suggests that cobalt may be active for ethylene reincorporation (the C2 fraction was almost entirely ethane) and may also form methane via ethylene cracking.

Although the activity of the cobalt catalyst dropped during the run, the alpha value based on C3 to C8 remained constant (0.76 in MB14 versus 0.77 in MB1). Values of alpha varied between 0.65 and 0.82 for most of the sets of conditions studied. However MB's 6-10 show a dramatic effect of CO conversion. At the high CO conversions (MB 6 and 7), lower molecular weight product is produced, indicated by the lower alpha values of 0.54 and 0.41 respectively. This is in contrast to the fused iron results where little change in alpha was observed over a wide range of conversions.

B. Secondary Reactions of Olefins

Dwyer and Somorjai in a paper that has been widely quoted (J. Catal., 56, 49 (1979)) report that upon the addition of ethylene or propylene to synthesis gas, the value of α over an iron film catalyst increased dramatically. This implies that the olefin is incorporated into the growing chains.

We have now performed similar detailed studies with ethylene or 1-butene, added to CO + H_2 on our fused iron catalyst. We can find no significant effect on alpha, contrary to Dwyer and Somorjai, but confirming an earlier scouting study of ours reported in the August-October quarterly. Some of the ethylene is hydrogenated to ethane, but little hydrogenation of the butene occurred. The reasons for the difference in results is not clear, but may reside in differences between the form of iron we used and that of Dwyer and Somorjai. Our results are being analyzed in more detail quantitatively.

C. Analytical Procedures

We have now prepared a detailed report on our analytical procedures entitled "A Stirred Autoclave Apparatus for Study of the Fischer-Tropsch Synthesis in a Slurry-Bed II. Analytical Procedures," by George A. Huff, Jr., Charles N. Satterfield, Martin H. Wolf. A copy is attached to this quarterly.

III. FUTURE WORK

The doctoral thesis of George A. Huff was accepted by M.I.T. on April 23, 1982. A summary of the thesis is being prepared and will be distributed with the next quarterly report. This covers most of our studies with the fused magnetite catalyst to date.

Work is continuing on developing a liquid chromatographic method for determining C-number distribution of the heavy wax product.

Reactor studies with precipitated iron are scheduled for the near future.

Determination of the product above about C_{15} is complicated by the fact that it is produced in small mole quantities and because of its low volatility it can accumulate significantly in the liquid in the reactor. We are making some theoretical analyses of how the heavy material in the overhead, which is what we analyze, may vary with time and these will be presented in the next quarterly.

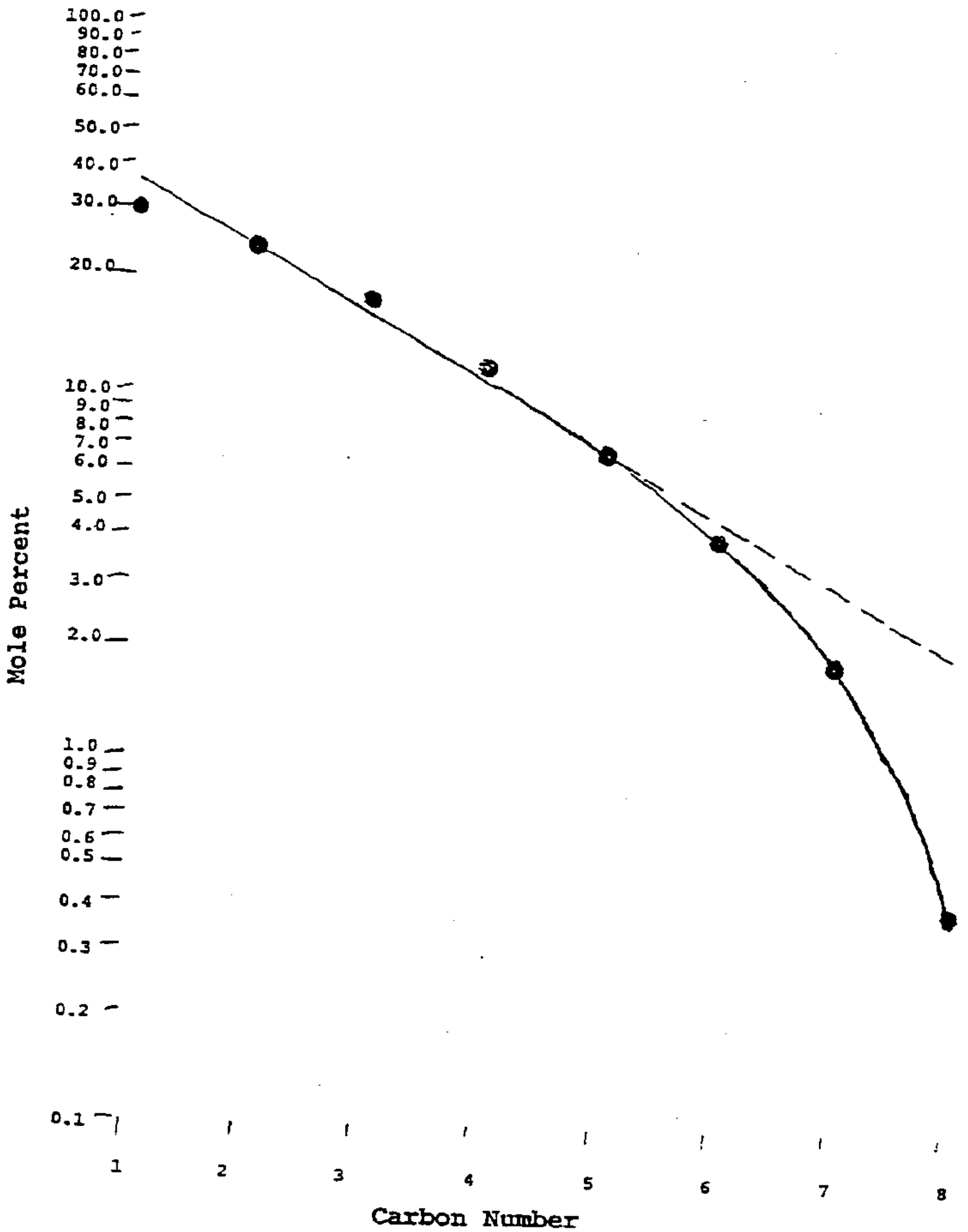

Figure 1 Schulz-Flory Plot for Iron at 285°C

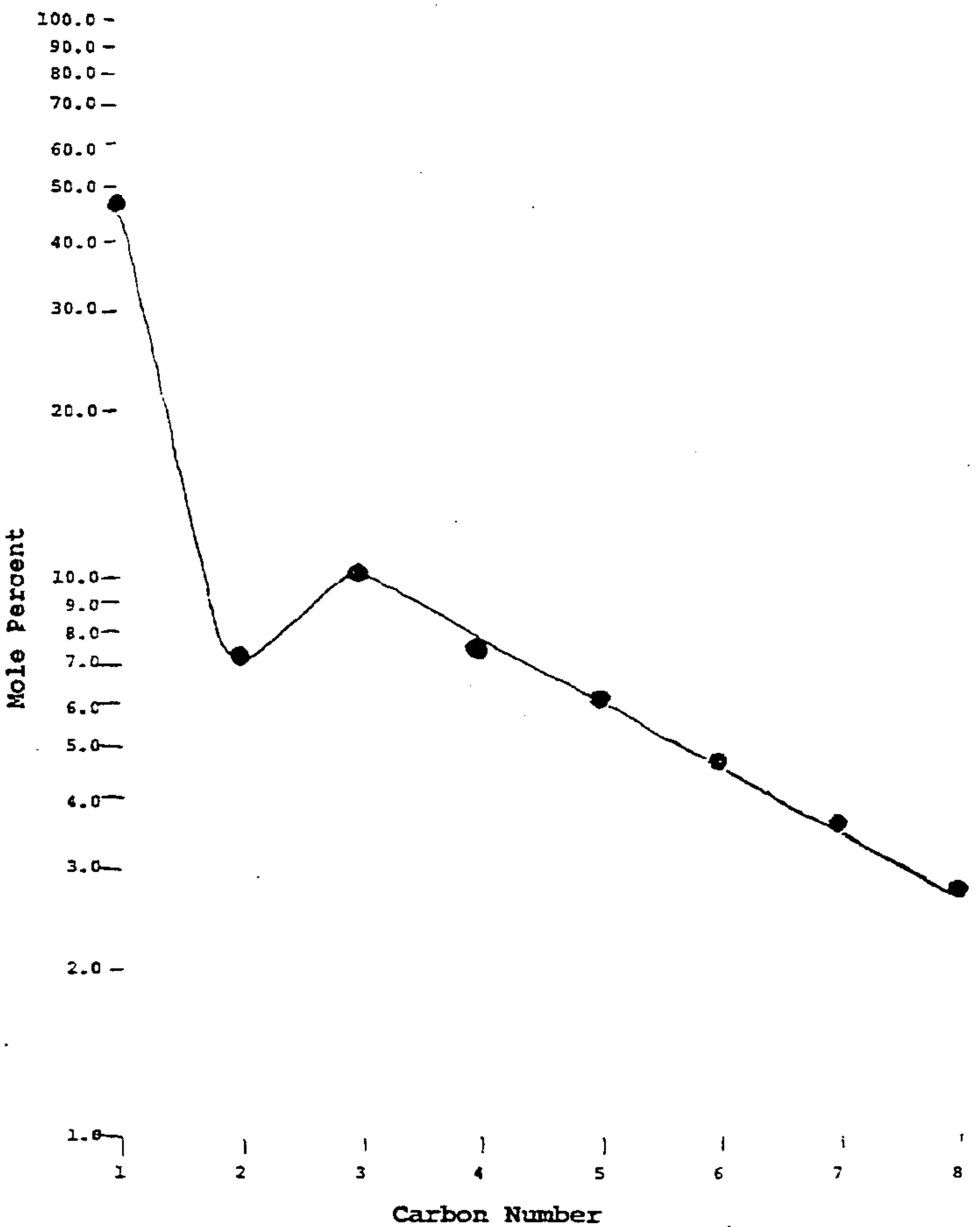

Figure 2 Schulz-Flory Plot for Cobalt Products From Material Balance 2

TABLE 1

Temp (C)	Pressure PSIG	Flow in l/m	Feed H_2/CO	Conversion $CO+H_2$ (%)	Use Ratio H_2/CO	Oxygen wt (%)	CH_4 wt (%)
285	100	.997	.514	80.10	.48	4.61	12.96

TABLE 2

MB#	T (C)	P PSIG	Flow in l/m	H_2 (%)	Conversion CO (%)	$CO+H_2$ (%)	Alpha
1	200	50	.658	50.6	45.9	48.9	.77
2	200	50	1.010	33.1	28.3	31.3	.76
3	200	100	.661	55.5	52.3	54.3	.73
4	200	28	.654	37.9	52.3	36.0	.73
5	200	50	1.390	21.8	17.8	20.4	.82
6	226	50	.661	87.8	93.9	89.9	.54
7	226	100	.659	89.2	96.6	91.8	.41
8	226	28	.664	75.1	74.0	74.7	.68
9	226	50	1.420	64.9	58.7	62.6	.73
10	226	50	1.040	74.2	69.6	72.5	.79
11	176	100	.665	10.1	8.0	9.3	.66
12	176	50	.669	9.1	7.8	8.6	.71
13	176	50	.478	10.9	8.7	10.1	.67
14	200	50	.671	39.2	34.7	37.5	.76
15	176	50	.628	8.5	4.6	6.4	.70
16	200	100	.640	36.5	17.2	26.3	.69
17	225	28	.638	64.1	33.1	47.6	.76
18	225	50	.639	70.7	37.4	53.0	.78
19	225	100	.639	78.5	43.5	59.9	.77
20	225	28	.640	61.9	31.2	45.6	.80

MB's 1 to 14 Feed = 1.74 H_2/CO
MB's 15 to 20 Feed = 0.88 H_2/CO