iron catalysts. Table 7 compares the activity of several precipitated and fused magnetite catalysts at or near 260°C. Alkalized precipitated catalysts prepared by Mobil (Kuo, 1983, 1985) and PETC, the Pittsburgh Energy Technology Center (Zarochak, McDonald, and Rao,1987), seem to have the highest activity. A United Catalysts C-73 fused magnetite ammonia synthesis catalyst run in our reactor (Huff, 1982) and elsewhere (Bukur and Brown, 1987) shows somewhat lower activity than the Ruhrchemie catalyst on the basis above. However, if the rate is assumed to have a first-order dependence on hydrogen pressure, the C-73 catalyst is more active than the Ruhrchemie catalyst. This comparison is somewhat limited from a fundamental point of view. The basis is total catalyst rather than iron loading and no information on surface area of the reduced catalysts is available.

The relatively high potassium loading of the Ruhrchemie catalyst (1.94 wt%) may lower activity somewhat, as suggested by data presented by Dry (1981) for SASOL precipitated iron catalysts. Dry shows that silica supported Fe_2O_3 promoted by K_2O decreases in activity with increased potassium loading, simultaneously undergoing a shift to heavier products. Since SASOL low temperature reactors are designed to produce hard wax and diesel fuel, it may be that somewhat lower activity is acceptable and may be compensated for by higher pressure operation.

2.3 Water-Gas Shift Activity

The Ruhrchemie catalyst does not appear to be very active for the water-gas shift reaction. Table 7 also compares water-gas shift activity, in the form of reaction quotients:

$$RQ = [CO_2][H_2]/[CO][H_2O] \qquad (6)$$

The reaction quotients for water-gas shift on the Ruhrchemie catalyst are very low relative to the Mobil and PETC catalysts; however, there is an alternative measure of water-gas shift activity which presents a more intuitively obvious sense of the relative activity of these catalysts.

If we consider the extent of water-gas shift, we write the reaction:

$$CO + H_2O \prec\!=\!=\!\succ CO_2 + H_2 \qquad (7)$$

The equilibrium is far to the right at temperatures of interest here so we may meaningfully use the concept of the extent of reaction as represented by:

$$X_{WGS} = P_{CO_2} / (P_{CO_2} + P_{H_2O}) \qquad (8)$$

This formulation excludes the effects of H_2 and CO, which are also consumed by the primary synthesis. For the Ruhrchemie catalyst, the extent of the water-gas shift reaction as defined by Eq. 8 at 263°C is about 35%, as compared to about 90% for the United Catalysts C-73 catalyst (Huff, 1982).

2.4 Hydrogenation Kinetics and Activity

Section 1.2.1.3 on the dependence of 1-alkene/n-alkane ratio on hydrogen partial pressure summarizes the hydrogenation kinetics and activity data obtained using this catalyst. The

rate of n-butane production is shown to be first-order in both hydrogen and 1-butene.

References

Anderson, R.B., The Fischer-Tropsch Synthesis, Academic Press, Orlando (1984).

Anderson, R.B., in Catalysis, 4 (P.H. Emmett, ed.), Rheinhold, New York (1956).

Anderson, R.B., F.S. Karn, and J.F. Shultz, Kinetics of the Fischer-Tropsch Synthesis on Iron Catalysts, Bulletin 614, United States Bureau of Mines (1964).

Bukur, D.B. and R.F. Brown, Can. J. Chem. Eng., 65, 604 (1987).

Dictor, R.A. and A.T. Bell, J. Cat., 97, 121 (1986).

Donnelly, T.J., I.C. Yates, and C.N. Satterfield, Energy and Fuels (in press).

Dry, M.E., Ind. Eng. Chem. Prod. Res. Dev., 15 (4), 282 (1976).

Dry, M.E., in Catalysis Science and Technology, Vol. 1 (J.R. Anderson and M. Boudart, eds.), Springer-Verlag, New York (1981).

Dry, M.E., The SASOL Fischer-Tropsch Processes, Appl. Ind. Cat., 2, 167 (1983).

Egiebor, N.O., Cooper, W.C., and Wojciechowski, B.W., Can. J. Chem. Eng., 63, 826 (1985).

Frohning, C.D. (private communication).

Frohning, C.D., Fischer-Tropsch-Synthese, Chemierohstoffe aus Kohle (J. Falbe, ed.), Stuttgart (1977).

Frohning, C.D., H. Kölbel, M. Ralek, W. Rottig, F. Schnur, and H. Schulz, in Chemical Feedstocks from Coal, (J. Falbe, ed.), Wiley, New York (1982).

Hanlon, R.T., Catalyst Characterization and Secondary Reaction Effects in Iron-catalyzed Fischer-Tropsch Synthesis, Sc. D. thesis, Massachusetts Institute of Technology (1985).

Hanlon, R.T. and C.N. Satterfield, Energy Fuels, 2 (2), 196 (1988).

Huff, G.A., Fischer-Tropsch Synthesis in a Slurry Reactor, Sc.D. thesis, Massachusetts Institute of Technology (1982).

Huff, G.A. and C.N. Satterfield, Ind. Eng. Chem. Fund., 21, 479 (1982).

Huff, G.A., C.N. Satterfield, and M.H. Wolf, Ind. Eng. Chem. Fund., 22, 258 (1983).

Huff, G.A. and C.N. Satterfield, J. Cat., 85, 370 (1984a).

Huff, G.A. and C.N. Satterfield, Ind. Eng. Chem. Proc. Des. Dev., 23, 696 (1984b).

Kuo, J.C.W., Slurry Fischer-Tropsch/Mobil Two-Stage Process of Converting Syngas to High Octane Gasoline, Final Report, DOE/PC/30022-10 (DE84004411), 1983.

Kuo, J.C.W., Two-Stage Process for Conversion of Synthesis Gas to High Quality Transportation Fuels, Final Report, DOE/PC/60019-9 (1985).

Matsumoto, D.K., Effects of Selected Process Variables on Performance of an Iron Fischer-Tropsch Catalyst, Sc. D. thesis, Massachusetts Institute of Technology (1987).

Satterfield, C.N., et al., Ind. Eng. Chem. Prod. Res.Dev., 25, 401 (1986).

Satterfield, C.N. and H.G. Stenger, Ind. Eng. Chem. Proc. Des. Dev., 23, 26 (1984).

Schulz, H., Rao, B.R., and Elstner, M., Erdol. Kohle, 23, 651 (1970).

Stenger, H.G., Johnson, H.E., and Satterfield, C.N., J. Cat., 86, 477 (1984).

Sudheimer, G. and J. Gaube, Ger. Chem. Eng., 8, 195 (1985).

Vannice, M.A., Catal. Rev. Sci. Eng., 14, 153 (1976).

Weitkamp, A.W., H.S. Seelig, N.J. Bowman, and W.E. Cady, Ind. Eng. Chem., 45, 343 (1953).

Zarochak, M.F., M.A. McDonald, and V.U.S. Rao, "Stability and Selectivity of Potassium Promoted Iron Catalyst in Slurry Fischer-Tropsch Synthesis", 12th Annual Conference on Fuel Sciences, Palo Alto, May 13-14, 1987.

Table 1

Composition of Ruhrchemie Precipitated Iron Catalyst

Fe	47.30 wt%
Cu	2.36
K	1.94
SiO_2	12.69
Al	0.02
Ca	0.08
C	0.16
H	1.09
O	34.36
Total	100.00

All compositions determined by atomic absorption spectrospcopy by Galbraith Laboratories, except oxygen by difference.

Table 2

Summary of Selectivity Information

MB	T °C	Qo	X	Clos.	C4OP	Cl mol.	Oxy	Alpha 1	Alpha 2	Slct.Alp.
1	232	0.555								
2	232	0.557								
3	232	0.548								
4	232	0.536								
5	248	0.554	30.1	98.9	3.8	0.226	3.8			0.705
6	248	0.363	28.2	97.7	3.8	0.217	7.4	0.69	0.92	0.714
7	248	0.361	34.7	97.5	4.0					
8	248	0.862	22.0	99.1	3.7	0.233	6.5	0.69	0.92	0.756
9	248	0.556								0.685
10	248	0.562	25.5	101.9	4.2		4.8			0.703
11	248	0.559	29.0	101.7	3.9	0.201	5.0	0.86	0.90	0.738
12	232	0.560	18.5	98.4	3.1	0.206	8.3	0.83	0.90	0.761
13	232	0.557				0.207		0.77	0.91	0.733
14	263	0.559	41.4	103.9	4.7	0.270	8.2	0.63	0.89	0.658
15	263	0.365	52.4	97.6	4.6	0.276	6.1	0.64	0.89	0.658
16	263	0.860	33.6	99.1	4.5	0.258	8.9	0.66	0.91	0.684
17	263	0.852								
18	248	0.554								
19	248	0.555	30.2	98.5	4.0	0.232	8.7	0.66	0.89	0.694
20	248	0.359								
21	263	0.362	57.5	100.0	4.4	0.240	4.6	0.67	0.91	0.666
22	263	0.862	38.6	96.4	4.3	0.209	5.6	0.80	0.90	0.719
23	263	0.558				0.242		0.64	0.90	0.677
24	232	0.556	26.7	95.9	3.2					
25	248	0.559	37.6	95.9	4.0	0.243	9.0	0.60	0.89	
26	248	0.352								
27	248	0.854	28.2	97.8	3.8	0.217	7.4	0.64	0.91	0.701
28	263	0.368	65.7	97.5	4.2	0.253				0.641
29	263	0.555	52.5	97.4	4.4	0.235	4.8	0.70	0.90	0.696
30	263	0.853	39.7	99.4	4.3	0.255	7.6	0.64	0.91	0.659
31	248	0.560	33.6	98.1	3.9	0.240	9.3	0.62	0.92	0.650
32	248	0.363	43.9	98.6	3.9	0.228	7.9	0.58	0.89	0.637
33	248	0.850	25.0	98.3	3.7	0.210	7.6	0.66	0.91	0.695
34	263	0.860	39.7	98.4	4.2		9.3			0.673
35	263	0.560	50.7	98.9	4.2	0.240	5.8	0.64	0.90	0.662

Q_o	Flow rate, Nl/min
X	Percent conversion of CO + H_2
Clos	Oxygen balance closure
C4OP	1-butene/n-butane
Cl mol.	Mol % CH_4
Oxy	wt % oxygenates
Alpha 1, Alpha 2	Calculated by non-linear regression, C_1-C_{16}
Slct. Alpha	Calculated by linear regression, C_3-C_7

Table 3

Component Chain Growth Probabilities

	MB 16		MB 23	
Component	α_1	α_2	α_1	α_2
1-alkene	0.67	0.78	0.63	0.78
n-alkane	0.73	0.93	0.71	0.93
oxygenates	0.52	--	0.52	--
Total	0.66	0.91	0.64	0.90

Table 4

Catalyst Selectivity Comparison

	Ruhrchemie	PETC[1]	Mobil[2] low wax	Mobil[3] high wax	UC C-73[4]	SASOL[5] fixed bed	PETC[6] no K	PETC[7] -1% K
Wt% Selectivity								
C_1	5.7	5.1	8.0	2.6	11.6	5.0	10.2	5.3
$C_2 - C_4$	27.0	26.9	22.7	9.2	39.6	12.6	32.4	23.1
$C_5 - C_{12}$	40.0	42.9	39.7	14.2	39.5	22.5	39.8	34.1
C_{12}^+	27.3	31.1	29.6	70.5	9.3	56.0	17.6	37.5
α_1	0.66		0.85	0.79	0.63	0.64	0.64	0.68
α_2	0.91		0.94	0.97	0.90	0.93	0.88	0.93
Conditions								
Temp., °C	263	260	262	249	263	220-250	260	260
Press., MPa	2.41	1.3	1.5	1.5	1.0	2.5	1.5	1.5
Flow, Nl/h/gcat	2.0	2.4	2.1	2.4	1.0		2.2	2.2
X_{CO+H2}	33.6	72.2	84.3	86.3	77.0		25.1	14.9

1. Zarochak, et. al. (1987).

2. Kuo (1983).

3. Kuo (1985).

4. Huff (1982).

5. Caldwell (1980)

6. Unalkalized precipitated iron catalyst prepared by PETC and tested in our lab.

7. Same as (6), but after addition of potassium tert-butoxide as promoter. Details on (6) and (7) are given in a separate report.

Table 5

Kinetic Data for 1-butene Hydrogenation

NB	T	Qo	Press FT	Press	C4 Press	C4 ole	C4 par	FT mol	C1 rt	RC4p/PC4o	RC4p/PH2
1	232	0.555			0.00E+00					ERR	ERR
2	232	0.557			0.00E+00					ERR	ERR
3	232	0.548			0.00E+00					ERR	ERR
4	232	0.536			0.00E+00					ERR	ERR
5	248	0.554	2721	38.9	9.44E-04	2.43	0.63	2.84E-04	6.42E-05	1.91E-06	2.05E-04
6	248	0.363	2722	58.9	2.33E-03	3.96	0.98	2.20E-04	4.77E-05	9.22E-07	2.45E-04
7	248	0.361	2720	59.2	1.88E-03	3.16	0.79	2.69E-04	0.00E+00	1.13E-06	2.51E-04
8	248	0.862	2722	30.6	5.80E-04	1.90	0.51	3.26E-04	7.60E-05	2.87E-06	1.76E-04
9	248	0.556	3025	49.7	1.36E-03	2.75	0.78	3.26E-04	0.00E+00	1.85E-06	ERR
10	248	0.562	2197	35.1	7.44E-04	2.12	0.51	3.35E-04	0.00E+00	2.28E-06	ERR
11	248	0.559	2722	50.9	1.47E-03	2.88	0.74	3.80E-04	7.64E-05	1.93E-06	3.24E-04
12	232	0.560	2722	20.3	2.13E-04	1.05	0.33	1.48E-04	3.05E-05	2.32E-06	5.06E-05
13	232	0.557	2722	23.0	3.12E-04	1.36	0.43	1.67E-04	3.46E-05	2.31E-06	7.42E-05
14	263	0.559	2721	92.1	6.31E-03	6.85	1.47	5.87E-04	1.58E-04	1.37E-06	1.08E-03
15	263	0.365	2722	127.0	1.27E-02	9.99	2.18	4.79E-04	1.32E-04	8.22E-07	1.37E-03
16	263	0.360	2722	70.7	3.54E-03	5.81	1.11	7.66E-04	1.98E-04	2.40E-06	9.81E-04
17	263	0.852			0.00E+00				0.00E+00	ERR	ERR
18	248	0.554			0.00E+00				0.00E+00	ERR	ERR
19	248	0.555	2723	53.3	2.08E-03	3.91	0.99	3.73E-04	8.65E-05	1.77E-06	4.11E-04
20	248	0.359			0.00E+00				0.00E+00	ERR	ERR
21	263	0.362	2722	161.3	1.77E-02	10.95	2.48	6.08E-04	1.46E-04	8.35E-07	2.09E-03
22	263	0.862	1481	49.9	1.50E-03	3.00	0.70	9.85E-04	2.06E-04	4.63E-06	7.49E-04
23	263	0.558	2998	140.5	1.39E-02	9.89	2.26	7.77E-04	1.88E-04	1.26E-06	2.12E-03
24	232	0.556			0.00E+00				0.00E+00	ERR	ERR
25	248	0.559			0.00E+00				0.00E+00	ERR	0.00E+00
26	248	0.352			0.00E+00				0.00E+00	ERR	ERR
27	248	0.854	2722	45.4	1.31E-03	2.90	0.76	5.05E-04	1.10E-04	2.93E-06	4.37E-04
28	263	0.368			0.00E+00				0.00E+00	ERR	ERR
29	263	0.555	2721	132.4	1.14E-02	8.62	1.95	8.02E-04	1.88E-04	1.37E-06	2.14E-03
30	263	0.853	2722	88.2	5.62E-03	6.37	1.47	9.00E-04	2.30E-04	2.36E-06	1.63E-03
31	248	0.560	2722	53.8	1.93E-03	3.59	0.93	3.81E-04	9.16E-05	1.83E-06	4.18E-04
32	248	0.363	2721	78.4	4.39E-03	5.60	1.42	3.30E-04	7.52E-05	1.07E-06	5.98E-04
33	248	0.850	2722	43.1	1.13E-03	2.61	0.72	5.01E-04	1.05E-04	3.18E-06	3.96E-04
34	263	0.860	2722	84.1	4.52E-03	5.37	1.27	8.86E-04	0.00E+00	2.49E-06	1.37E-03
35	263	0.560	2723	115.1	8.95E-03	7.78	1.85	7.19E-04	1.73E-04	1.49E-06	1.77E-03

T, °C

Q_o Flow rate, Nl/min

Press. in kPa

FT Press. HC + Oxygenates, kPa

C_4 Press. For 1-butene, kPa

C_4 ole,
C_4 par Mol % in Fischer-Tropsch products

F-T mol Rate, mols Fischer-Tropsch products per minute

C_1 rt Rate of formation, mols/min

RC4p/PC4o Rate of formation, n-butane in m. mol/min/g. cat divided by pressure of 1-butene, MPa

RC4p/pH_2 Same, divided by H_2 pressure

Table 6

Summary of Kinetic Information

NR	T	Qo	XH2	XCO	DegRt	PH2	PCO	PH2O	PCO2	WGS I	Rate
1	232	0.555				0.000	0.000	0.000	0.000	ERR	0.000
2	232	0.557				0.000	0.000	0.000	0.000	ERR	0.000
3	232	0.548				0.000	0.000	0.000	0.000	ERR	0.000
4	232	0.536				0.000	0.000	0.000	0.000	ERR	0.000
5	248	0.554	37.53	24.70	0.515410	0.871	1.438	0.177	0.136	0.434	0.298
6	248	0.363	35.28	23.29	0.514650	0.871	1.476	0.137	0.132	0.492	0.183
7	248	0.361	42.52	29.13	0.505382	0.842	1.416	0.158	0.188	0.543	0.224
8	248	0.862	28.46	17.20	0.536662	0.935	1.481	0.140	0.075	0.348	0.339
9	248	0.556	37.88	24.99	0.514813	0.000	0.000	0.000	0.152	1.000	0.000
10	248	0.562	34.41	18.78	0.561800	0.000	0.000	0.000	0.088	1.000	0.256
11	248	0.559	38.72	21.64	0.556047	0.863	1.453	0.158	0.135	0.469	0.289
12	232	0.560	24.75	13.85	0.555733	0.964	1.513	0.110	0.048	0.293	0.185
13	232	0.557	26.36	11.97	0.611010	0.960	1.521	0.106	0.051	0.327	0.000
14	263	0.559	47.87	36.43	0.479117	0.792	1.267	0.234	0.281	0.546	
15	263	0.365	56.99	48.91	0.449230	0.755	1.180	0.137	0.464	0.773	0.342
16	263	0.860	39.52	29.21	0.486408	0.858	1.376	0.170	0.186	0.522	0.516
17	263	0.852				0.000	0.000	0.000	0.000	ERR	0.000
18	248	0.554				0.000	0.000	0.000	0.000	ERR	0.000
19	248	0.555	39.03	23.50	0.537592	0.886	1.463	0.103	0.156	0.603	0.299
20	248	0.359				0.000	0.000	0.000	0.000	ERR	0.000
21	263	0.362	61.08	54.64	0.438991	0.715	1.067	0.184	0.556	0.772	0.372
22	263	0.862	45.91	32.93	0.493906	0.915	1.454	0.198	0.264	0.571	0.594
23	263	0.558	54.79	49.09	0.438605	0.822	1.267	0.233	0.471	0.670	0.000
24	232	0.556				0.000	0.000	0.000	0.000	ERR	0.265
25	248	0.559	42.41	34.26	0.484243	0.836	1.362	0.175	0.221	0.558	0.375
26	248	0.352	35.25	23.29	0.514650	0.000	0.000	0.000	0.000	ERR	0.000
27	248	0.854				0.871	1.476	0.137	0.132	0.492	0.430
28	263	0.368	66.11	65.40	0.414382	0.000	0.000	0.000	0.000	ERR	0.432
29	263	0.555	55.97	50.07	0.438985	0.724	1.172	0.161	0.473	0.745	0.520
30	263	0.853	44.38	36.00	0.466002	0.803	1.332	0.151	0.288	0.656	0.805
31	248	0.560	40.07	29.08	0.491148	0.840	1.420	0.159	0.190	0.543	0.336
32	248	0.363	49.03	40.26	0.460184	0.775	1.298	0.184	0.326	0.639	0.285
33	248	0.850	31.67	20.48	0.519801	0.896	1.490	0.165	0.116	0.412	0.379
34	263	0.860	44.44	36.36	0.461077	0.815	1.334	0.141	0.289	0.673	0.610
35	263	0.560	53.82	48.59	0.436729	0.744	1.182	0.165	0.459	0.735	0.507

Table 7

Catalyst Activity Comparison

	Ruhrchemie	PETC[1]	Mobil[2] low wax	Mobil[3] high wax	UC C-73[4]	PETC[5] no K	PETC[6] -1% K
Activity							
mmol/min/gcat	0.49	1.3	1.3	1.5	0.37	--	--
$\frac{\text{mmol/min}}{\text{gcat/atm}H_2}$	0.05				0.15	--	--
$\frac{[CO_2][H_2]}{[CO][H_2O]}$	1.0	20.0		39.0	40.0	--	--
Conditions							
Temp., °C	263	260	262	249	263	260	260
Press., MPa	2.41	1.3	1.5	1.5	1.0	1.5	1.5
Flow, Nl/h/gcat	2.0	2.4	2.1	2.4	1.0	2.2	2.2
X_{CO+H2}	33.6	72.2	84.3	86.3	77.0	25.1	14.9

1. Zarochak, et. al. (1987).

2. Kuo (1983).

3. Kuo (1985).

4. Huif (1982).

5. Unalkalized precipitated iron catalyst prepared by PETC and tested in our lab.

6. Same as (5), but after addition of potassium tert-butoxide as promoter. Details on (5) and (6) are given in a separate report.

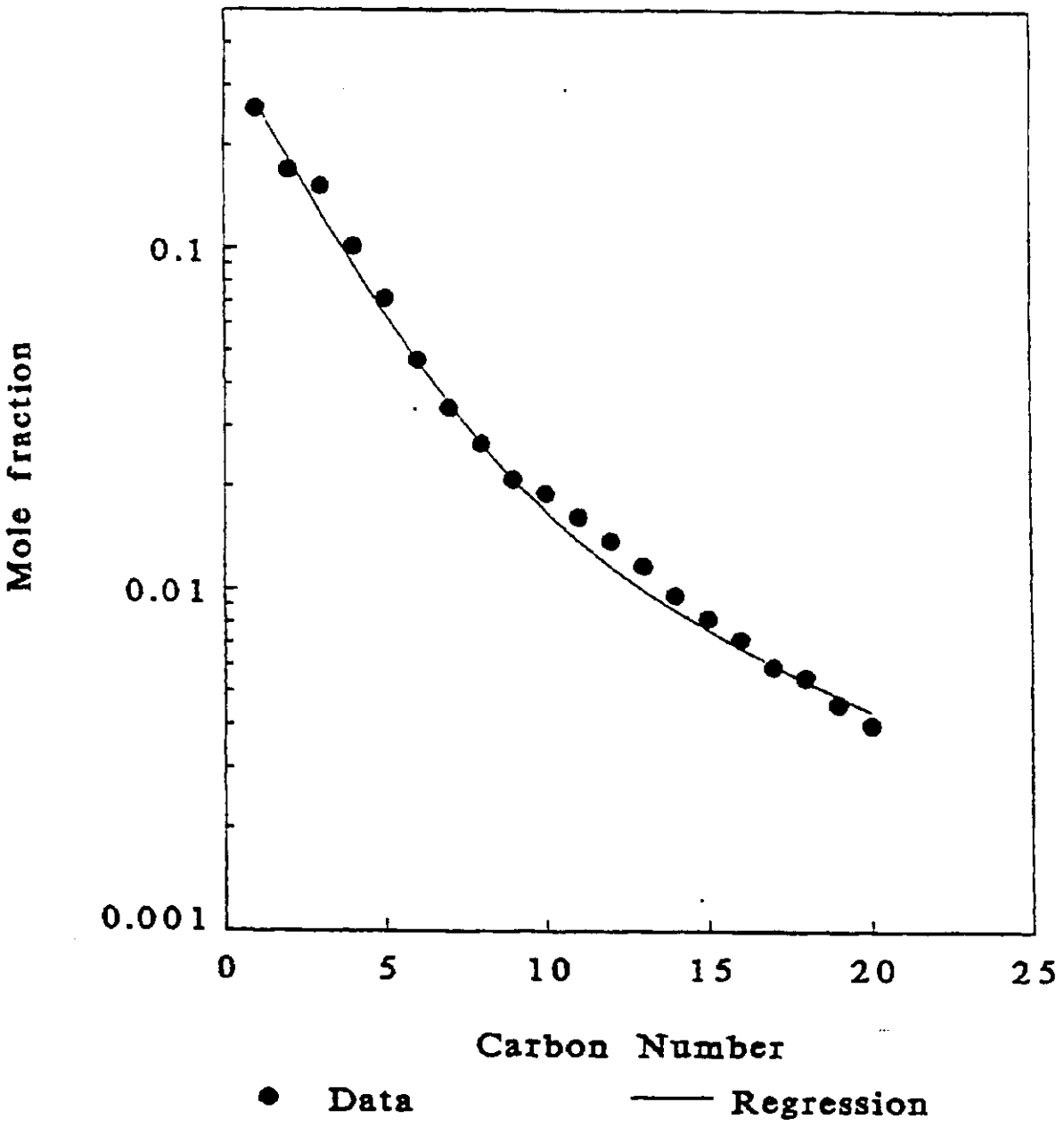

Figure 1
Schulz-Flory Diagram for MB 16
(263°C, 0.034 Nl/min/gcat, 2.4 MPa)

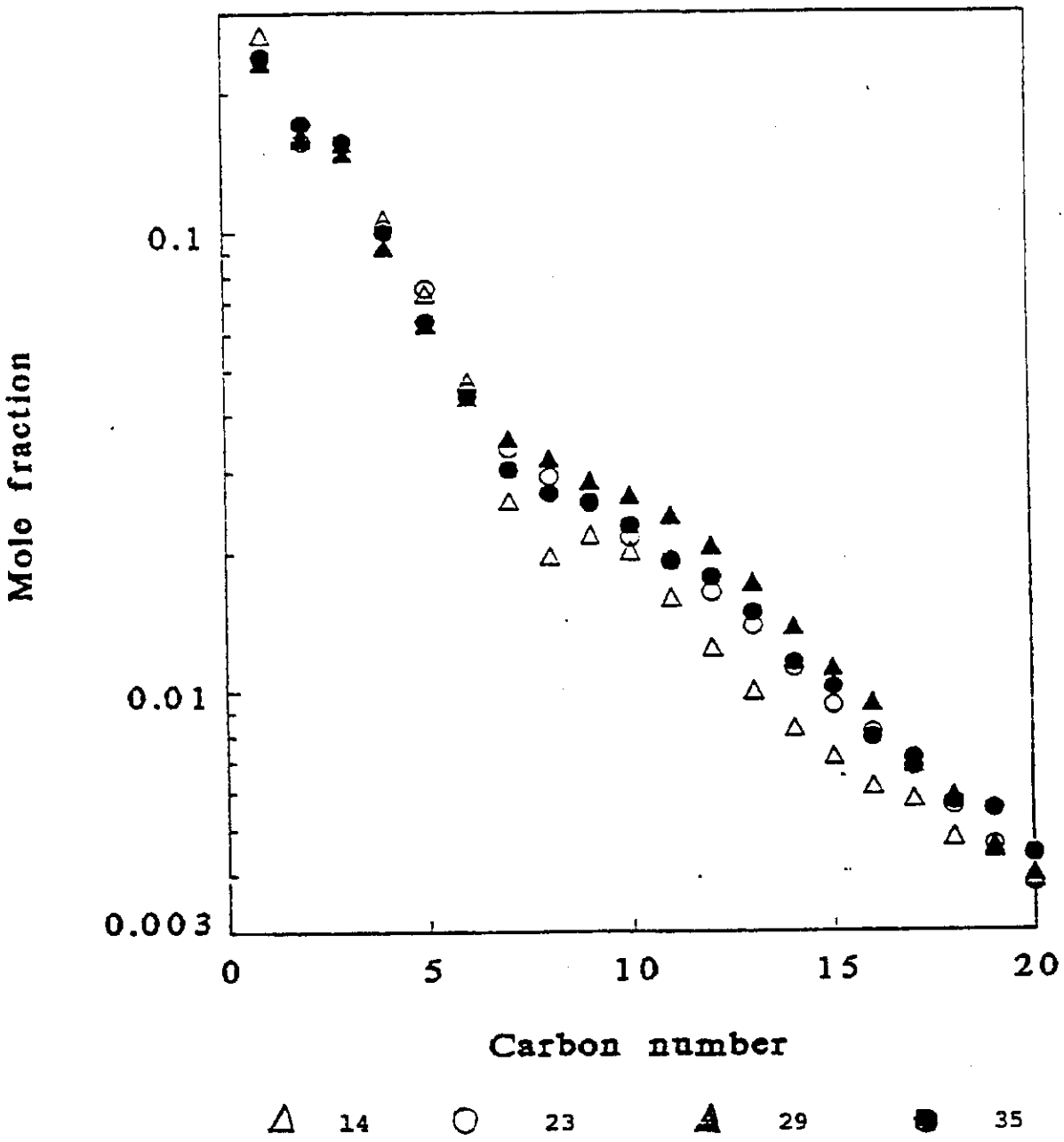

Figure 2
Comparative Schulz-Flory Diagram for
Material Balances at 263°C, 0.022 Nl/min/gcat
Pressure = 2.7 to 3.0 MPa

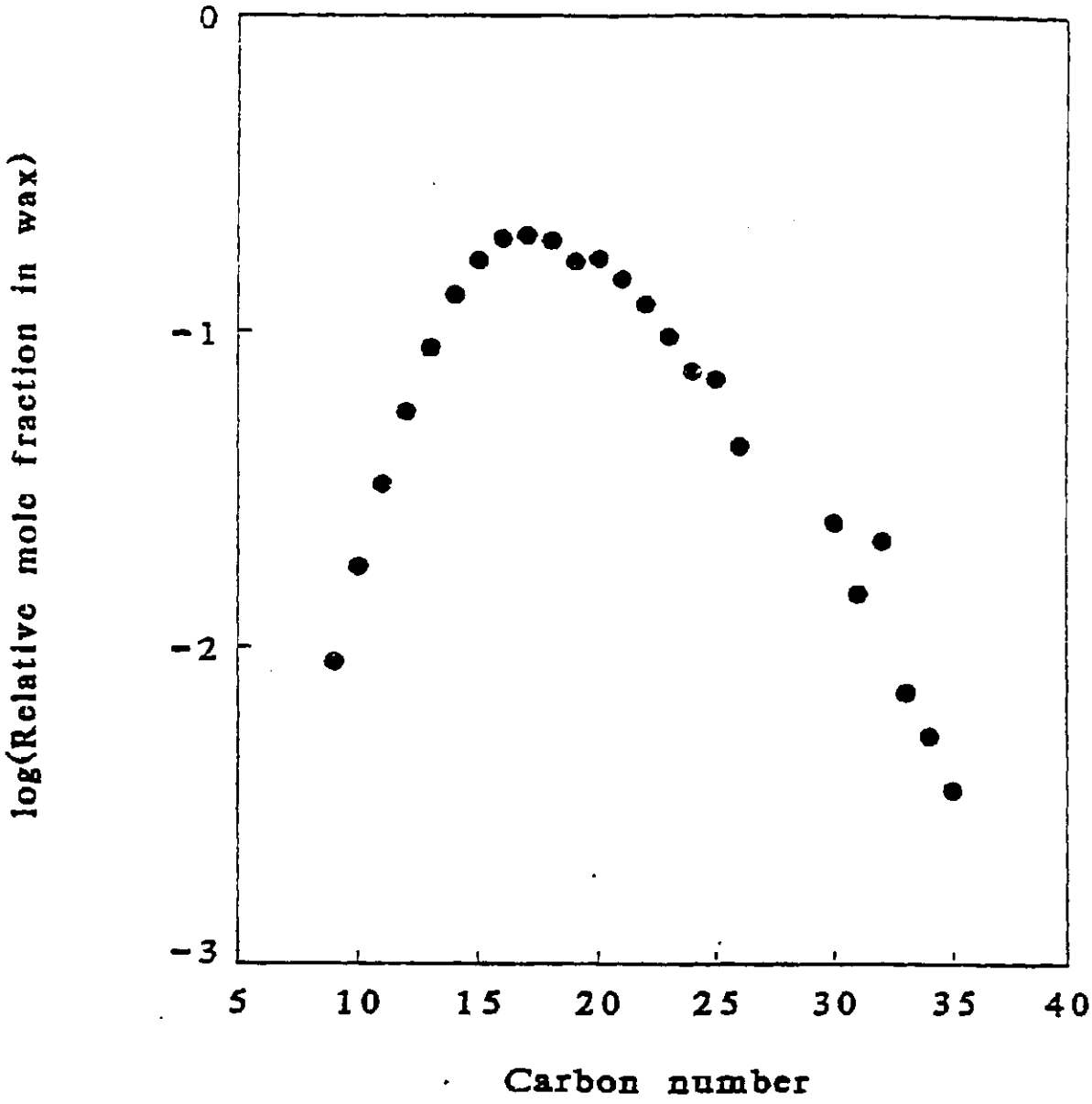

Figure 3
Schulz-Flory Diagram for Slurry Wax
After 150 Hours-on-Stream

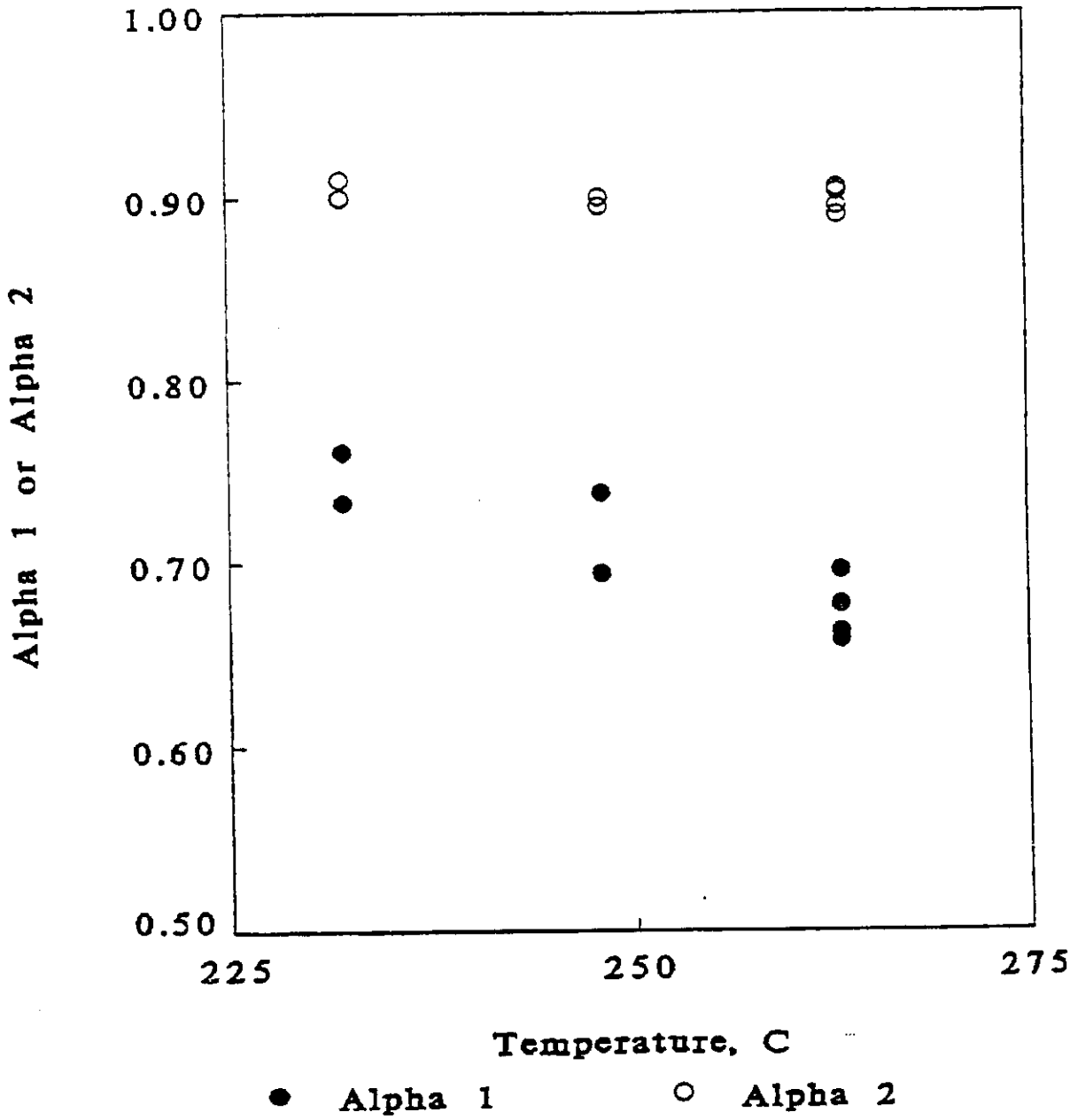

Figure 4
Temperature Dependence of α_1 and α_2
Space Velocity 0.022 Nl/min/gcat

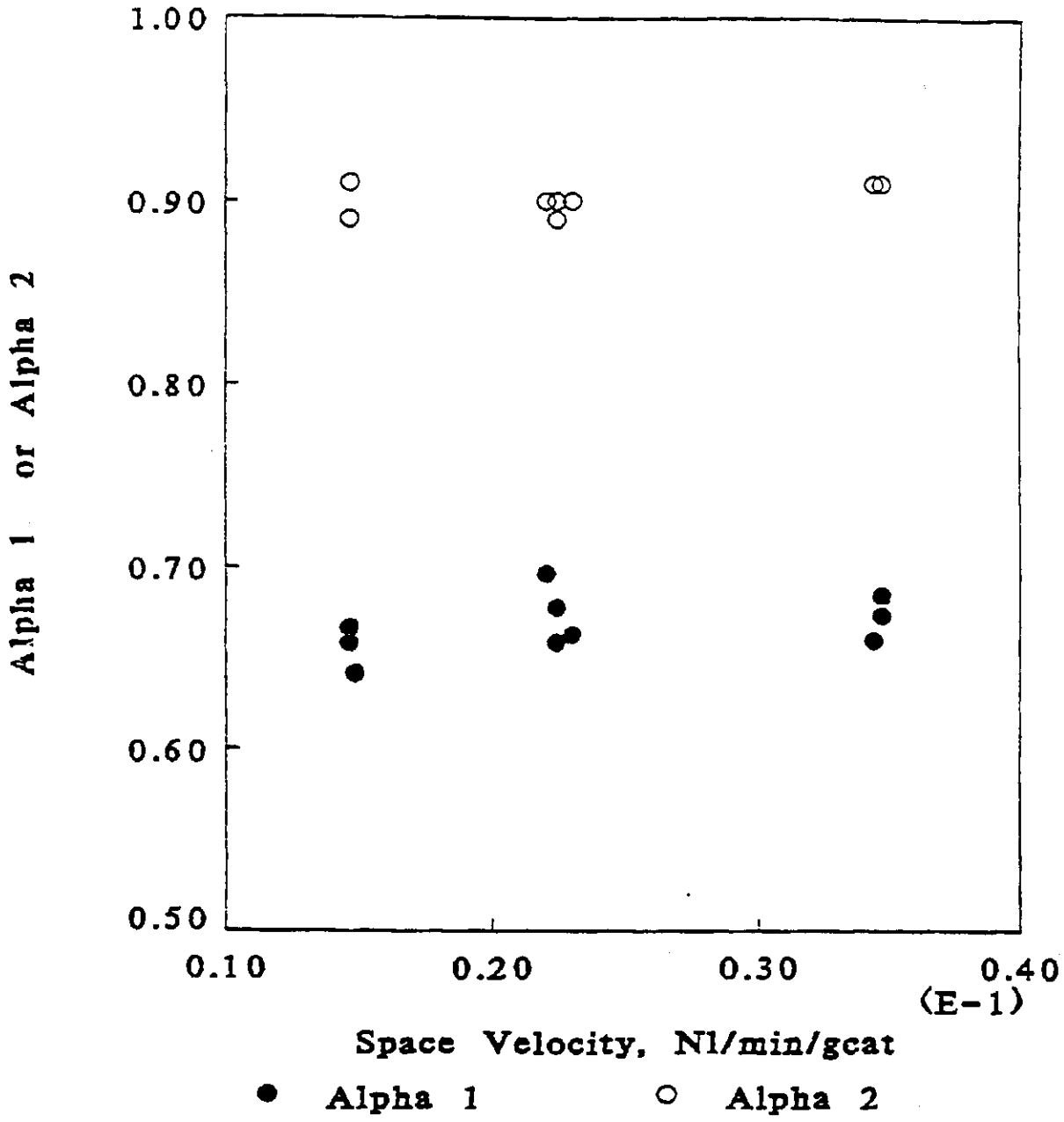

Figure 5
Space Velocity Dependence of α_1 and α_2
Temperature 248°C

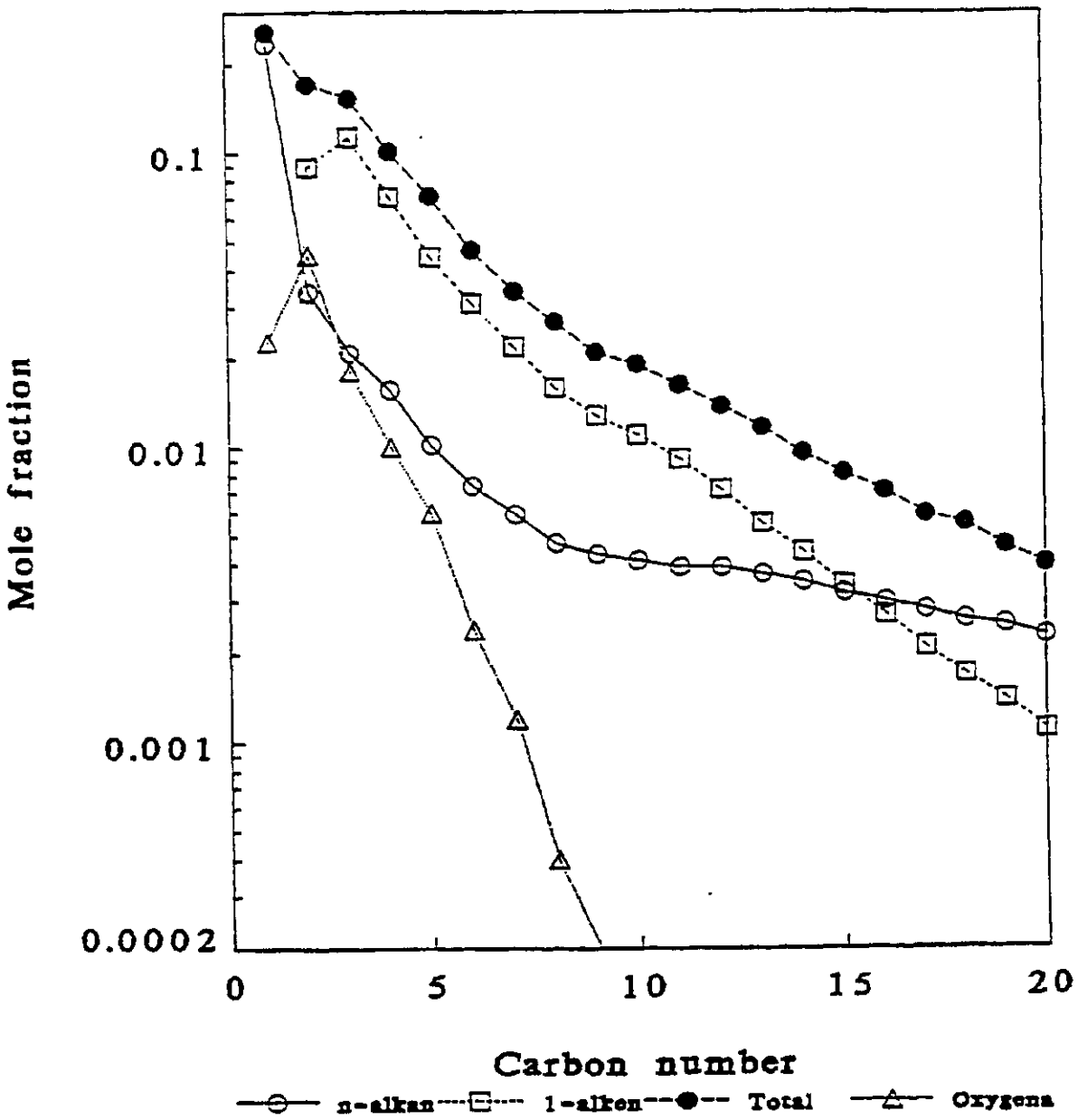

Figure 6
Component Schulz-Flory Diagram for MB 16
(263°C, 0.034 Nl/min/gcat, 2.4 MPa),
Overhead Products

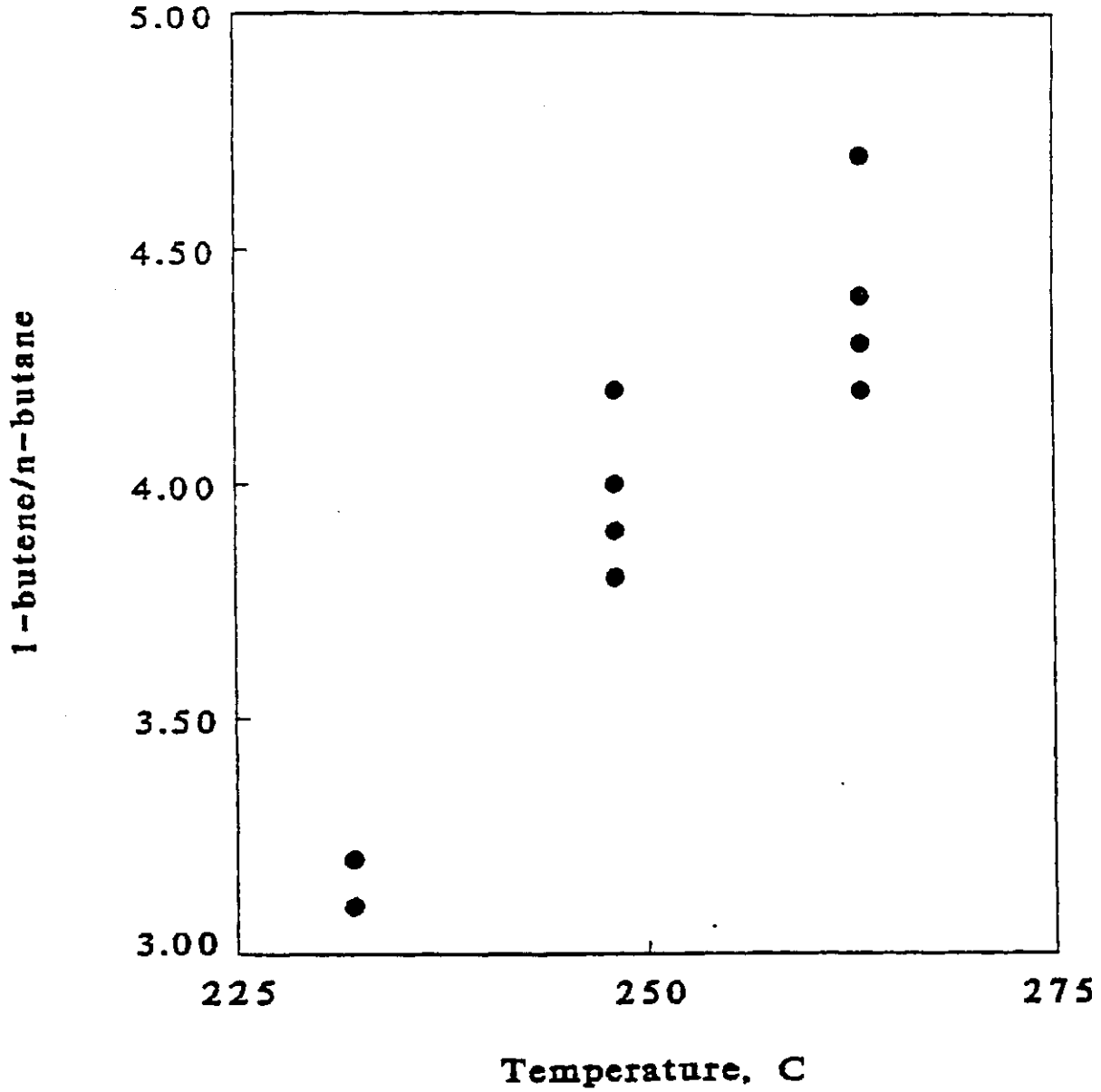

Figure 7
Temperature Dependence of 1-butene/n-butane
Space Velocity 0.022 Nl/min/gcat

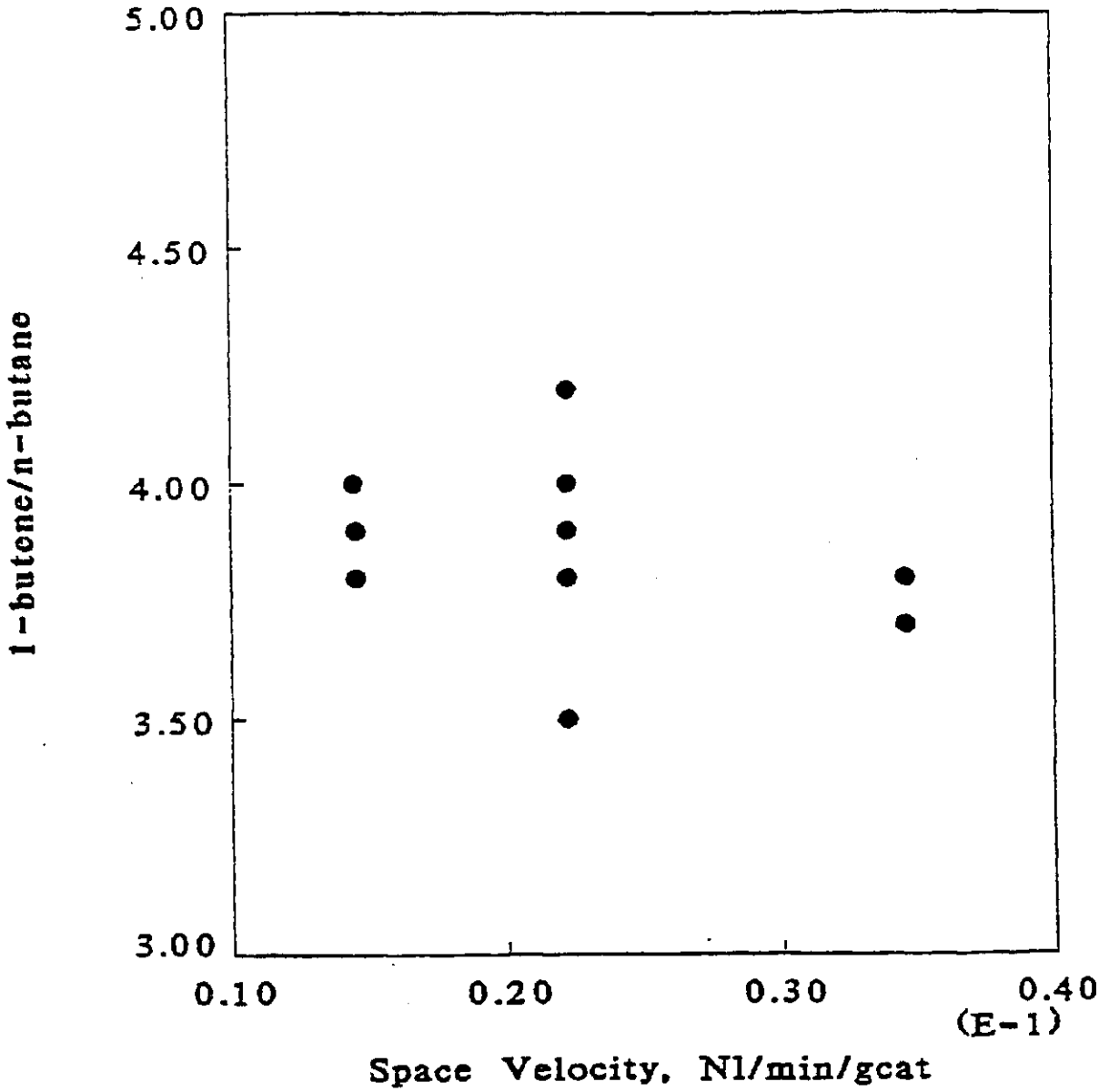

Figure 8
Space Velocity Dependence of 1-butene/n-butane
Temperature 248°C