Table 20. Specific Activities and Product Selectivities of Unsupported Cobalt (Reduced at 400°C) for Steady-State CO Hydrogenation at Different Pressures.

Run No.	Reaction Pressure (atm)	Reaction Tempeature °C	Reaction Time (hrs)	% CO Conversion	N_{CO}[a]x10^3	Product Selectivity Carbon Atom %[b] CO_2	H.C.	Wt. Frac. of Hydrocarbon Product[c] C_1	C_2-C_4	C_5-C_{11}	C_{12}^+	Alcs.	Propagation Probability α	Eact. (kJ/mole)
43	1	180	20	1.17	0.18	7.0	93.0	18.0	26.2	42.2	13.5	0	0.772	106
44	1	190	30	1.97	0.30	7.3	92.7	20.0	27.5	40.6	11.9	0	0.771	
45	1	195	43	2.62	0.41	8.5	91.5	25.6	33.1	39.9	1.4	0	0.713	
46	1	200	50	3.70	0.57	7.6	92.4	25.4	32.5	38.7	3.4	0	0.695	
47	1	210	64	3.21	1.0	9.1	90.9	31.7	34.5	33.0	0.8	0	0.667	
37	21	180	90	1.36	0.21	1.5	98.5	17.9	48.0	30.0	4.1	0	0.654	150
38	21	190	94	3.34	0.52	1.2	98.8	15.9	45.2	35.2	3.7	0	0.657	
39	21	195	99	6.04	0.94	0.9	99.1	14.9	43.6	37.1	4.4	0	0.666	
42	21	210	120	5.38	2.5	1.3	98.7	18.4	42.8	33.4	5.4	0	0.645	

[a]CO Turnover frequency defined as CO molecules converted per catalytic site per second.

[b]Based on total CO converted.

[c]Weight percentage of hydrocarbon groups based on total hydrocarbons in the product.

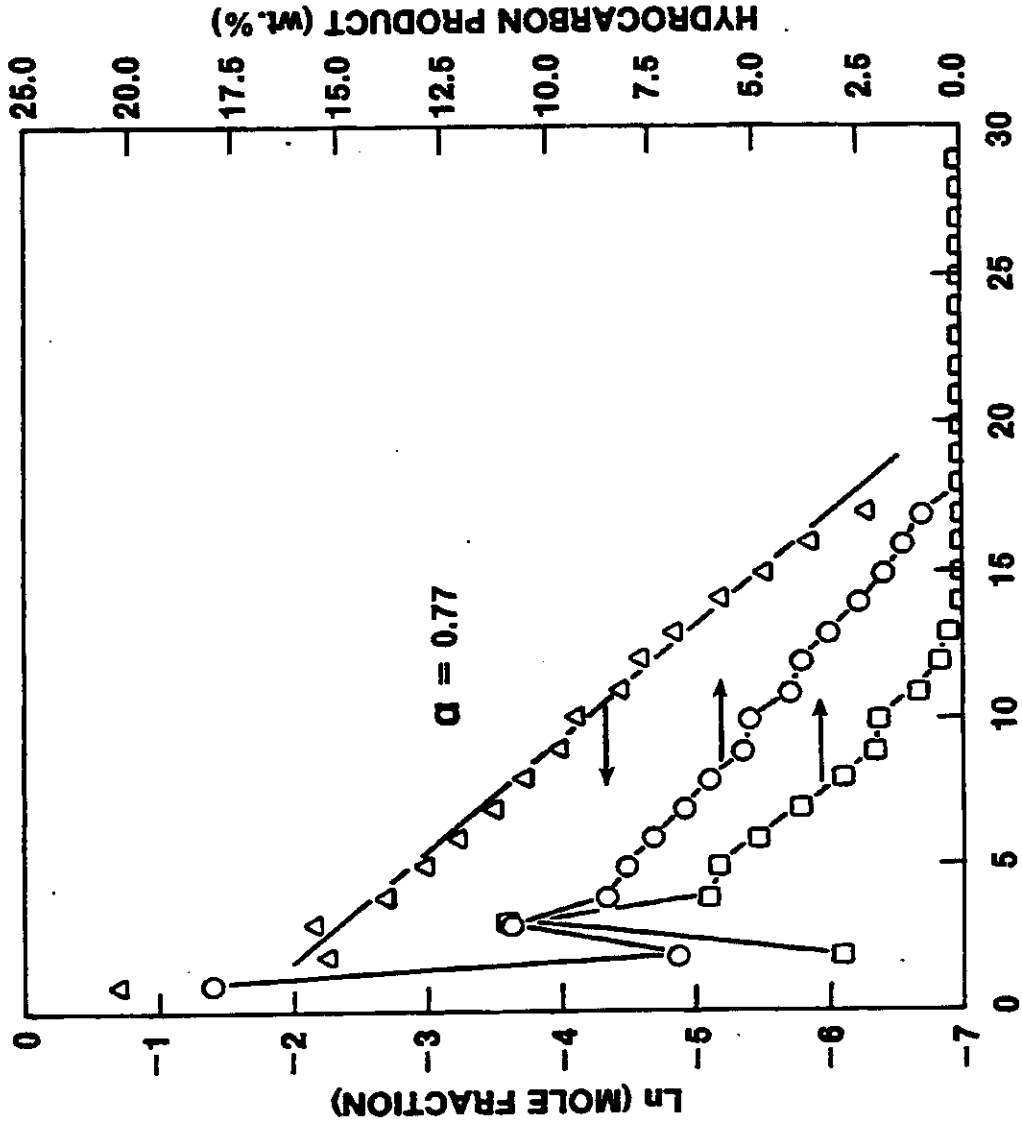

Fig. 16. ASF plot and product distribution for Co at 453 K and 1 atm.

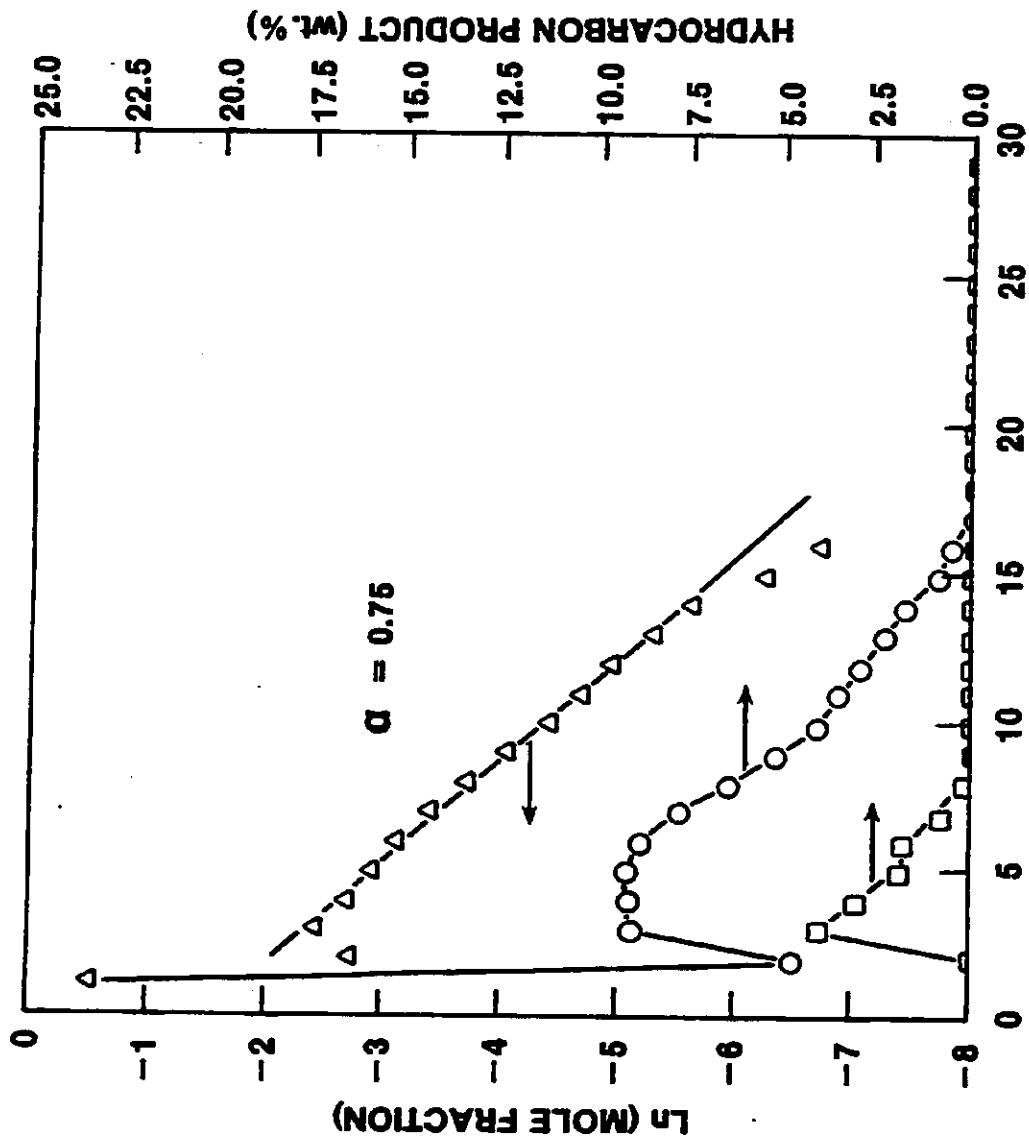

Fig. 17. ASF plot and product distribution for CoB (reduced 523 K) at 452 K, 1 atm.

During the twelfth quarter and the fourth year of the contract a relatively large number of activity/selectivity experiments were conducted to measure the CO hydrogenation activity and selectivity properties of cobalt and iron boride catalysts. Experiments were also conducted to determine effects of boron and sodium promoters and of alumina support on the steady state CO hydrogenation activity and selectivity of cobalt. These activity/selectivity data for cobalt and iron catalysts are summarized in Tables 21-31 and Figures 18-29. The results are more conveniently discussed in two subsections dealing separately with catalytic activity and selectivity.

a. Catalyst Activity. Specific activities in the form of CO turnover frequencies (N_{CO} the number of CO molecules converted per catalytic site per second) for steady state CO hydrogenation at 1 atm, $H_2/CO = 2$, and different reaction temperatures on unsupported and alumina-supported cobalt, borided cobalt, and sodium-promoted cobalt catalysts are listed in Table 21. Also included in this table are activation energies, E_{CO}, and activities in terms of moles of CO reacted per gram of catalyst per second, R_{CO}. Activities were measured after an initial stabilization period of at least 20 hours. Gas hourly space velocity and temperature were varied in order to maintain CO conversion close to 5% and within the range of 2-10%.

It is not possible to compare catalysts at the same temperature due to the large differences in activity between these catalysts and to the limitations of the catalytic reactor system. However, the Arrhenius plots presented in Figure 18 for unsupported catalysts show the effects of boron and sodium on specific activity, N_{CO}. It is evident that the boron-promoted cobalt, CoB-250, is a factor of ten more active than the unpromoted cobalt while addition of the sodium promoter Co/Na lowers the specific activity of cobalt by a factor of about 10. The sodium-containing borided cobalt, CoB/Na-250, is only slightly more active than the unpromoted cobalt, indicating that the effects of boron and sodium probably offset each other. CoB-109G prepared from gas-phase boriding with diborane/H_2 has a specific activity comparable to that of unpromoted cobalt. The activation energies for the boron-promoted cobalt catalysts, e.g. CoB-250, CoB/Na-250, and CoB-109G, are slightly higher relative to the pure cobalt catalyst. In contrast, the Co/Na catalyst has an activation energy that is twice as low as that of cobalt.

All the unsupported catalysts exhibited relatively stable activity after the initial stabilization period with the exception of Co/Na, for which catalyst deactivation was observed during reactor tests as shown in Figure 18. The deactivation was probably due to the formation of cobalt carbides in the course of reaction at high temperatures, as evidenced by the x-ray diffraction pattern of the Co/Na catalyst. The rate of CO conversion decreased in the order: CoB-250 > CoB/Na-250 > Co > CoB-109G > Co/Na.

Figure 19 displays the Arrhenius plots for alumina-supported catalysts. It is evident that the specific activity of boron-promoted CoB/Al_2O_3-250 is a factor of 30 higher than that of the 3% Co/Al_2O_3 containing no boron. The low specific activity observed on $CoB/Na/Al_2O_3$-250 is likely due to the presence of sodium with a Co/Na ratio of about 0.6, in contrast to 16 for unsupported CoB/Na. As compared with 3% Co/Al_2O_3, the activation energy of CoB/Al_2O_3-250 is higher while that of $CoB/Na/Al_2O_3$-250 is lower.

Comparison of Figures 18 and 19 reveals that CoB-250 has a specific

Table 21
Effects of Boron, Sodium and Alumina Support on the Steady-State CO Hydrogenation Activity of Cobalt Catalysts at Different Temperatures, 1 atm and $H_2/CO = 2$.

Catalyst Code	Temp. (°C)	S.V.[a] (hr^{-1})	% CO Conv.[a]	N_{CO}[b] x10^3 (s^{-1})	R_{CO}[c] x10^7 (mole/gcat•s)	E_{CO}[d] (KJ/mole)
CoB-250	156	165	4.91	1.35	0.47	95
	168	400	4.51	3.00	1.05	
	179	750	4.79	5.97	2.09	
	189	1600	3.29	8.76	3.07	
CoB/Na-250	170	300	6.13	0.23	0.56	115
	180	650	5.04	0.41	0.99	
	190	1100	6.16	0.85	2.05	
	200	2100	6.18	1.62	3.93	
Co-104	195	200	4.85	0.91	0.34	83
	210	300	6.44	1.81	0.67	
	225	500	6.95	3.26	1.21	
CoB-109G	212	600	1.94	1.13	0.26	117
	225	600	4.76	2.66	0.61	
	240	600	10.59	5.50	1.26	
Co/Na-100	260	240	4.15	0.96	0.37	40
	270	240	3.89	0.90	0.35	
	280	240	5.84	1.35	0.53	
	290	440	2.80	1.18	0.46	
	300	440	4.38	1.85	0.72	
CoB/Al_2O_3-250	170	300	3.80	4.71	0.64	105
	181	500	3.73	7.78	1.06	
	195	1400	3.70	21.40	2.91	
CoB/Na/Al_2O_3-250	238	300	7.00	2.42	1.22	79
	248	600	7.48	5.16	2.61	
	258	900	5.02	5.20	2.63	
	268	900	7.30	7.56	3.82	

[a] S.V. = gas hourly space velocity; Conv. = conversion
[b] CO turnover frequency in molecules of CO reacted per H adsorption site per second.
[c] Reaction rate in moles per gram of catalyst per second.
[d] Activation energy for CO conversion determined from temperature dependence of N_{CO}.

Table 22
Activity and Selectivity of Co-104 (Reduced in H_2 at 350 °C) for Steady-State CO Hydrogenation. H_2 : CO = 2

Run #	27	29	30	37	38	39	42
Temp. (°C)	195	210	225	180	190	195	210
P (atm.)	1	1	1	10	10	10	10
S.V. (hr^{-1})	200	300	500	165	165	165	500
CO conv. (%)	4.85	6.44	6.95	1.36	3.34	6.04	5.38
$N_{CO} \times 10^3$ (TOF)[a]	0.91	1.81	3.26	0.21	0.52	0.94	2.50
$R_{CO} \times 10^7$ (mol/g·s)	0.34	0.67	1.21	0.08	0.19	0.35	0.94
Duration (hrs.)	30	60	75	100	125	140	150
Product Selectivity based on CO Converted (Carbon Atom%)							
CO_2	3.5	3.6	5.5	1.5	1.2	0.9	1.3
Hydrocarbons	96.5	96.4	94.5	98.5	98.8	99.1	98.7
Distribution of Total Hydrocarbons (wt %)							
C_1	21.7	26.7	34.7	17.9	15.9	14.9	18.4
C_2-C_4	26.4	35.1	37.3	48.0	45.2	43.6	42.8
C_5-C_{11}	41.3	35.8	27.3	30.0	35.2	37.1	33.4
C_{12}^+	10.6	2.4	0.6	4.1	3.7	4.4	5.4
Total Olefin Content for each Carbon Number (mol %)[b]							
C_2	15	10	13	42	28	23	25
C_3	58	60	64	60	70	69	72
C_4	57 [74]	55 [60]	60 [60]	57 [96]	56 [93]	59 [91]	62 [96]
C_5	44 [49]	37 [42]	43 [34]	58 [95]	54 [88]	54 [89]	53 [89]
C_6	34 [40]	32 [32]	34 [31]	56 [93]	49 [89]	49 [86]	52 [89]
C_7	21 [33]	19 [25]	17 [25]	41 [89]	47 [88]	44 [84]	49 [88]
α (propag. proba.)	0.728	0.629	0.569	0.654	0.657	0.666	0.645
E_{CO} (kJ/mol)		82.5				150	

[a] CO Turnover Frequency is defined as CO molecules reacted per site per second.
[b] Value in [ ] for C_4 to C_7 denotes percentage of a-olefin/total olefin.

Table 23
Activity and Selectivity of CoB-250 catalyst
(Reduced in H_2 at 250°C)
for Steady-State CO Hydrogenation. H_2: CO = 2

Run #	4	5	6	7	10	9	11	12
Temp. (°C)	156	168	179	189	144	157	168	179
P (atm.)	1	1	1	1	10	10	10	10
S.V. (hr^{-1})	165	400	750	1600	165	350	800	1600
CO conv. (%)	4.91	4.51	4.79	3.29	5.71	4.17	3.59	4.34
$N_{CO} \times 10^3$ (TOF)[a]	1.35	3.00	5.97	8.76	1.57	2.43	4.78	11.54
$R_{CO} \times 10^7$ (mol/g·s)	0.47	1.05	2.09	3.07	0.55	0.85	1.67	4.04
Duration (hrs.)	41	48	67	78	90	114	118	125
Product Selectivity based on CO Converted (Carbon Atom %)								
CO_2	1.1	1.2	0.9	1.1	0.4	0.8	0.6	0.6
Hydrocarbons	98.9	98.8	99.1	98.9	99.6	99.2	99.4	99.4
Distribution of Total Hydrocarbons (wt %)								
C_1	22.6	22.4	23.2	29.7	22.3	24.9	25.1	26.3
C_2-C_4	19.3	21.3	23.1	29.9	25.0	25.5	26.3	26.5
C_5-C_{11}	43.9	45.3	45.1	38.8	41.6	37.4	35.8	36.4
C_{12}^+	14.2	11.0	8.6	1.6	11.1	12.2	12.8	10.8
Total Olefin Content for each Carbon Number (mol %)[b]								
C_2	0	0	2	4	0	0	9	0
C_3	47	50	46	49	54	53	60	55
C_4	$^{35}_{[64]}$	$^{36}_{[64]}$	$^{34}_{[56]}$	$^{38}_{[59]}$	$^{41}_{[83]}$	$^{44}_{[84]}$	$^{46}_{[93}$	$^{49}_{[85]}$
C_5	$^{20}_{[52]}$	$^{25}_{[49]}$	$^{21}_{[46]}$	$^{24}_{[50]}$	$^{35}_{[63]}$	$^{40}_{[52]}$	$^{44}_{[79]}$	$^{43}_{[55]}$
C_6	$^{20}_{[22]}$	$^{21}_{[26]}$	$^{21}_{[24]}$	$^{23}_{[26]}$	$^{29}_{[42]}$	$^{34}_{[42]}$	$^{43}_{[55]}$	$^{36}_{[54]}$
C_7	$^{10}_{[17]}$	$^{10}_{[22]}$	$^{10}_{[21]}$	$^{12}_{[24]}$	$^{21}_{[42]}$	$^{23}_{[38]}$	$^{31}_{[52]}$	$^{26}_{[52]}$
α (propag. proba.)	0.796	0.770	0.746	0.652	0.764	0.778	0.788	0.764
E_{CO} (kJ/mol)			95				89	

[a] CO Turnover frequency defined as CO molecules reacted per site per second.

[b] Value in [ ] for C_4 to C_7 denotes percentage of a-olefin/total olefin.

Table 24
Activity and Selectivity of CoB-109G (Red. in H_2 at 350 ^oC) for Steady-State CO Hydrogenation. H_2: CO = 2, P = 1 atm

Run #	6	10	11
Temp. (^oC)	212	225	240
S.V. (hr^{-1})	600	600	600
CO conv. (%)	1.94	4.76	10.59
$N_{CO} \times 10^3$ (TOF)[a]	1.13	2.66	5.50
$R_{CO} \times 10^7$ (mol/g.s)	0.26	0.61	1.26
Duration (hrs.)	28	50	70
Product Selectivity based on CO Converted (Carbon Atom%)			
CO_2	4.2	4.2	3.5
Hydrocarbons	95.8	95.8	96.5
Distribution of Total Hydrocarbons (wt %)			
C_1	39.8	44.7	59.3
C_2-C_4	31.9	34.1	30.0
C_5-C_{11}	27.5	21.0	10.6
C_{12}^+	0.8	0.2	0.1
Total Olefin Content for each Carbon Number (mol %)[b]			
C_2	11	2	0
C_3	100	62	31
C_4	68 [71]	58 [51]	52 [44]
C_5	53 [51]	42 [36]	38 [22]
C_6	47 [36]	35 [20]	31 [18]
C_7	38 [23]	4 [0]	0 [0]
α (propag. proba.)	0.589	0.517	0.440
E_{CO} (KJ/mol)		116.7	

[a] CO Turnover frequency defined as CO molecules reacted per site per second.
[b] Value in [ ] for C_4 to C_7 denotes percentage of a-olefin/total olefin.

Table 25
Activity and Selectivity of CoB/Na-250
(Reduced in H_2 at 250 °C)
for Steady-State CO Hydrogenation. H_2: CO = 2

Run #	8	11	13	14	18	24	22	23
Temp. (°C)	170	180	190	200	170	180	190	200
P (atm.)	1	1	1	1	10	10	10	10
S.V. (hr^{-1})	300	650	1100	2100	750	1350	2400	4500
CO conv. (%)	6.13	5.04	6.16	6.18	4.33	5.53	7.78	9.14
$N_{CO} \times 10^3$ (TOF)[a]	0.23	0.41	0.85	1.62	0.41	0.93	2.34	5.14
$R_{CO} \times 10^7$ (mol/g·s)	0.56	0.99	2.05	3.93	0.98	2.26	5.65	12.44
Duration (hrs.)	118	145	165	174	42	91	76	80
Product Selectivity based on CO Converted (Carbon Atom%)								
CO_2	2.4	3.0	2.6	2.7	2.1	2.8	2.6	2.7
Hydrocarbons	97.6	97.0	97.4	97.3	97.9	97.2	97.4	97.3
Distribution of Total Hydrocarbons (wt %)								
C_1	25.1	22.4	22.1	23.5	35.4	25.3	23.9	22.5
C_2-C_4	19.8	20.7	23.9	24.1	39.7	41.3	38.0	36.0
C_5-C_{11}	50.6	50.5	50.7	47.7	24.7	32.0	35.5	39.0
C_{12}^+	4.6	6.4	3.4	4.7	0.2	1.5	2.6	2.6
Total Olefin Content for each Carbon Number (mol %)[b]								
C_2	0	0	13	11	14	16	10	11
C_3	65	71	71	70	29	49	41	43
C_4	$^{41}_{[84]}$	$^{49}_{[90]}$	$^{52}_{[80]}$	$^{52}_{[79]}$	$^{20}_{[100]}$	$^{30}_{[99]}$	$^{24}_{[98]}$	$^{28}_{[97]}$
C_5	$^{36}_{[59]}$	$^{43}_{[75]}$	$^{45}_{[65]}$	$^{44}_{[61]}$	$^{22}_{[94]}$	$^{35}_{[78]}$	$^{23}_{[89]}$	$^{26}_{[90]}$
C_6	$^{27}_{[46]}$	$^{34}_{[56]}$	$^{35}_{[50]}$	$^{36}_{[46]}$	$^{15}_{[95]}$	$^{26}_{[84]}$	$^{21}_{[81]}$	$^{24}_{[82]}$
C_7	$^{20}_{[32]}$	$^{26}_{[41]}$	$^{27}_{[37]}$	$^{27}_{[35]}$	$^{25}_{[100]}$	$^{25}_{[94]}$	$^{24}_{[84]}$	$^{26}_{[84]}$
α (propag. proba.)	0.788	0.773	0.750	0.725	0.559	0.596	0.636	0.649
E_{CO} (kJ/mol)			115				148	

[a] CO Turnover frequency defined as CO molecules reacted per site per second.
[b] Value in [ ] for C_4 to C_7 denotes percentage of a-olefin/total olefin.

Table 26
Activity and Selectivity of Co/Na-100 (Red. in H_2 at 350 °C)
for Steady-State CO Hydrogenation. H_2: CO = 2, P = 1 atm

Run #	1	2	3	4	5
Temp. (°C)	260	270	280	290	300
S.V. (hr^{-1})	240	240	240	440	440
CO conv. (%)	4.15	3.89	5.84	2.80	4.38
$N_{CO} \times 10^3$ (TOF)[a]	0.96	0.90	1.35	1.18	1.85
$R_{CO} \times 10^7$ (mol/g.s)	0.37	0.35	0.53	0.46	0.72
Duration (hrs.)	18	35	41	63	73
Product Selectivity based on CO Converted (Carbon Atom%)					
CO_2	73.8	69.1	69.1	66.0	63.6
Hydrocarbons	26.2	30.9	30.9	34.0	36.4
Distribution of Total Hydrocarbons (wt %)					
C_1	51.0	46.7	46.9	48.2	50.9
C_2-C_4	48.2	53.0	51.3	50.9	48.8
C_5-C_{11}	0.8	0.3	1.8	0.9	0.3
C_{12}^+	0	0	0	0	0
Total Olefin Content for each Carbon Number (mol %)					
C_2	58	68	85	82	92
C_3	100	100	100	100	100
C_4	59	95	92	84	85
α (propag. proba.)	0.341	0.335	0.337	0.310	0.297
E_{CO} (KJ/mol)			40.3		

[a] CO Turnover frequency defined as CO molecules reacted per site per second.

Table 27
Activity and Selectivity of $CoB-Al_2O_3-250$
(Reduced in H_2 at 250 °C)
for Steady-State CO Hydrogenation. H_2: CO = 2

Run #	13	14	15	16	20	26	30
Temp. (°C)	170	181	181	195	170	181	195
P (atm.)	1	1	1	1	10	10	10
S.V. (hr^{-1})	300	300	500	1400	500	700	1600
CO conv. (%)	3.8	7.4	3.7	3.7	2.6	4.0	3.8
$N_{CO} \times 10^3$ (TOF)[a]	4.7	9.3	7.8	21.4	5.4	11.6	25.3
$R_{CO} \times 10^7$ (mol/g·s)	0.64	1.26	1.06	2.91	0.73	1.57	3.44
Duration (hrs.)	48	55	67	73	32	44	55
Product Selectivity based on CO Converted (Carbon Atom%)							
CO_2	0.8	0.7	0.7	0.8	0	0.5	0.5
Hydrocarbons	99.2	99.3	99.3	99.2	100	99.5	99.5
Distribution of Total Hydrocarbons (wt %)							
C_1	13.8	16.5	16.1	20.1	25.8	21.2	24.5
C_2-C_4	12.3	16.7	15.7	18.3	23.1	16.5	14.7
C_5-C_{11}	59.4	57.2	56.9	50.7	47.7	50.4	51.1
C_{12}^+	14.5	9.7	11.4	10.9	3.4	11.9	9.7
Total Olefin Content for each Carbon Number (mol %)[b]							
C_2	0	0	0	0	0	0	0
C_3	47	45	65	35	54	67	61
C_4	37 [75]	38 [48]	41 [67]	43 [66]	54 [93]	53 [84]	50 [86]
C_5	31 [57]	33 [28]	33 [56]	32 [55]	52 [91]	50 [75]	50 [78]
C_6	30 [28]	29 [16]	32 [27]	33 [27]	49 [57]	40 [61]	36 [80]
C_7	18 [23]	16 [15]	20 [21]	21 [20]	30 [53]	26 [53]	26 [71]
α (propag. proba.)	0.822	0.759	0.766	0.756	0.748	0.815	0.824
E_{CO} (kJ/mol)			105			107	

[a] CO Turnover frequency defined as CO molecules reacted per site per second.
[b] Value in [ ] for C_4 to C_7 denotes percentage of a-olefin/total olefin.

Table 28
Activity and Selectivity of $CoB-Al_2O_3-250$
(Reduced in H_2 at 250 °C)
for Steady-State CO Hydrogenation. P = 1 atm.

Run #	32	33	15	35	36
Temp. (°C)	181	181	181	181	181
H_2 : CO	4	3	2	1	0.5
S.V. (hr^{-1})	800	650	500	350	200
CO conv. (%)	5.5	4.4	3.7	2.5	1.9
$N_{CO} \times 10^3$ (TOF)[a]	11.1	9.0	7.8	5.5	3.2
$R_{CO} \times 10^7$ (mol/g·s)	1.51	1.23	1.06	0.75	0.43
Duration (hrs.)	13	16	67	33	37
Product Selectivity based on CO Converted (Carbon Atom%)					
CO_2	0	0.4	0.7	1.2	2.0
Hydrocarbons	100	99.6	99.3	98.8	98
Distribution of Total Hydrocarbons (wt %)					
C_1	23.0	20.2	16.1	11.3	8.2
C_2-C_4	20.8	19.2	15.7	11.5	12.2
C_5-C_{11}	49.3	53.1	56.9	60.9	62.9
C_{12}^+	6.9	7.5	11.4	16.3	16.7
Total Olefin Content for each Carbon Number (mol %)[b]					
C_2	0	0	0	18	0
C_3	38	48	65	100	100
C_4	$27_{[51]}$	$31_{[59]}$	$41_{[67]}$	$55_{[84]}$	$63_{[90]}$
C_5	$22_{[35]}$	$25_{[46]}$	$33_{[56]}$	$48_{[74]}$	$65_{[78]}$
C_6	$25_{[13]}$	$28_{[18]}$	$32_{[27]}$	$45_{[42]}$	$61_{[48]}$
C_7	$12_{[13]}$	$15_{[16]}$	$20_{[21]}$	$32_{[30]}$	$43_{[39]}$
α (propag. proba.)	0.704	0.723	0.766	0.821	0.833

[a] CO Turnover frequency defined as CO molecules reacted per site per second.
[b] Value in [ ] for C_4 to C_7 denotes percentage of a-olefin/total olefin.

Table 29
Activity and Selectivity of CoB/Na-Al_2O_3-250
(Red. in H_2 at 250 °C)
for Steady-State CO Hydrogenation. H_2: CO = 2

Run #	1	2	3	4	6	7	8
Temp. (°C)	238	248	258	268	238	248	258
P (atm.)	1	1	1	1	10	10	10
S.V. (hr^{-1})	300	600	900	900	300	600	900
CO conv. (%)	7.00	7.48	5.02	7.30	10.12	9.31	10.87
$N_{CO} \times 10^3$ (TOF)[a]	2.42	5.16	5.20	7.56	3.49	6.42	11.26
$R_{CO} \times 10^7$ (mol/g·s)	1.22	2.61	2.63	3.82	1.77	3.25	5.70
Duration (hrs.)	50	60	75	90	105	120	140
Product Selectivity based on CO Converted (Carbon Atom%)							
CO_2	50.3	56.4	57.2	58.9	59.1	59.4	58.4
Hydrocarbons	49.7	43.6	42.8	41.1	40.9	40.6	41.6
Distribution of Total Hydrocarbons (wt %)							
C_1	28.6	29.7	36.2	39.9	22.4	24.6	26.3
C_2-C_4	42.9	41.0	52.1	50.8	44.1	45.0	43.4
C_5-C_{11}	28.5	29.3	11.7	9.4	33.5	30.5	29.1
C_{12}^+	0	0	0	0	0	0	1.2
Total Olefin Content for each Carbon Number (mol %)[b]							
C_2	39	41	64	72	58	69	67
C_3	100	100	100	100	100	100	100
C_4	85 [43]	88 [38]	90 [66]	89 [74]	79 [94]	78 [96]	83 [94]
C_5	83 [38]	78 [37]	84 [60]	83 [65]	74 [92]	76 [93]	80 [90]
C_6	79 [33]	76 [29]	81 [53]	77 [59]	70 [80]	73 [93]	79 [85]
C_7	63 [23]	60 [21]	69 [51]	68 [50]	61 [78]	69 [90]	73 [77]
α (propag. proba.)	0.553	0.565	0.431	0.377	0.588	0.579	0.571
E_{CO} (kJ/mol)							

[a] CO Turnover frequency defined as CO molecules reacted per site per second.
[b] Value in [ ] for C_4 to C_7 denotes percentage of a-olefin/total olefin.

TABLE 30
Activities And Selectivities Of FeB2, FeB5 And Commercial FeB Catalysts During CO Hydrogenation At 21 ATM.

Catalyst	FeB2			FeB5			FeB-COM		
Reac. P (atm)	21	21	21	20	20	20	21	21	21
Reac. T (°C)	274	289	304	259	270	281	225	237	250
Dur. time (hr)	49	28	39	29	52	76	70	56	36
CO conv. (%)	2.2	3.8	6.2	4.1	4.1	2.6	2.6	6.1	6.9
TOF ($X 10^3$)[a]	.215	.373	.621	.396	.264	.254	2.7	8.5	21.5
Rco ($X 10^7$)[b]	0.35	0.61	1.00	0.96	0.64	0.61	0.05	0.15	0.39
Carbon atom %									
CO_2	11.7	10.9	15.1	7.1	8.2	10.2	8.0	9.1	9.9
Hydrocarbon	88.3	89.1	84.9	92.9	91.8	89.8	92.0	90.9	90.1
Wt. frac. of H.C.									
C_1	76.3	73.3	78.5	60.2	62.7	69.4	54.1	55	35.9
C_{2-4}	22.9	25.0	20.3	35.8	32.9	29.0	36.7	35.2	46.3
C_{5-11}	1.0	1.7	1.2	4.0	4.3	1.6	9.2	9.8	17.7
C_{12+}	0	0	0	0	0	0	0	0	0
Alcs	0.8	0	0.8	0	0.3	2.0	10.7	10.4	0
Olefin/Paraffin									
C_{2-4}	0.35	0.25	0.11	1.29	0.95	0.69	0.31	0.35	0.45
C_{3-7}	0.60	0.42	0.21	1.48	1.26	0.97	0.66	0.71	0.85
α(propag. prob.)		0.26	0.30	0.30	0.37	0.36	0.29	0.53	0.53
Olefin content[c] (mole %)									
C_2	19	15	7	53	48	36	8	11	7
C_3	45	37	18	66	65	61	38	41	47
C_4	12(40.9)	19(51.3)	18(26.1)	55(45)	55(30)	21(57.2)	52(17.2)	52(18.1)	53(25.3)
C_5	---	---	---	34(53)	53(15)	4	32(11.9)	30(8.9)	41(10.7)
C_6	---	---	---	36(28.6)	48(19)	---	11(18.3)	44(4.1)	41(5.7)
Ea (KJ/mole)	92.9			---			179		

a. Turnover frequency is defined as number of molecules of CO reacted per catalytic site per second.
b. Reaction rate is defined as number of moles of CO reacted per gram of catalyst per second.
c. Number in the parenthesis denotes the α-olefin content in the olefin.

TABLE 31
Activity And Selectivity Of Fe/B/Na During Hydrogenation At 10 And 21 ATM

Reac. P (atm)	10	10	10	10	21	21	21
Reac. T (^{o}C)	221	231	241	250	220	229	240
Dur. time (hr)	26	37	50	59	28	53	77
CO conv. (%)	4.6	6.2	5.6	4.9	6.9	7.6	8.7
TOF (X 10^3)[a]	2.82	3.83	5.15	6.84	6.18	14.1	32.1
Rco(mol/g.sec) (X 10^7)[b]	0.44	0.60	0.80	1.07	0.96	2.19	5.00
Carb. atom %							
CO_2	15.8	17.9	18.0	17.5	11.0	10.6	9.3
Hydrocarbon	84.2	82.1	82	82.5	89.0	89.4	90.7
Wt. frac. of H.C.							
C_1	41.0	41.8	45.7	49.5	38.9	39.7	41.2
C_{2-4}	46.2	45.6	43.4	40.9	41.4	41.8	41.6
C_{5-11}	12.8	12.7	10.6	9.5	19.0	17.9	16.3
C_{12+}	0	0	0.2	0.1	0.6	0.7	0.9
Alcs	1.4	0.7	0.6	1.3	10.2	8.2	7.4
Olefin/Paraffin							
C_{2-4}	1.31	1.21	1.24	1.31	1.08	1.07	1.13
C_{3-7}	2.40	2.44	2.74	2.61	1.47	1.46	1.76
α (propag. prob.)	0.52	0.49	0.47	0.44	0.54	0.53	0.52
Olefin content[c] (mole %)							
C_2	44	40	42	45	39	39	39
C_3	77	78	78	78	71	70	75
C_4	57(85)	61(81.5)	62(81.8)	61(82.1)	53(93.8)	53(60.1)	57(44.7)
C_5	75(41.6)	73(56.9)	81(36.8)	74(46.9)	44(94.1)	45(63.4)	46(60.0)
C_6	52(82)	51(58.5)	50(88.1)	52(80.3)	46(94.7)	45(68.4)	47(74.3)
C_7	35	34	38	38	36	33	38
Ea (KJ/mole)	65.4				172.7		

a. Turnover number is defined as number of molecules of CO reacted per catalytic site per second.
b. Reaction rate is defined as number of moles of CO reacted per gram of catalyst per second.
c. Number in the parenthesis denotes the α-olefin content in the olefin.

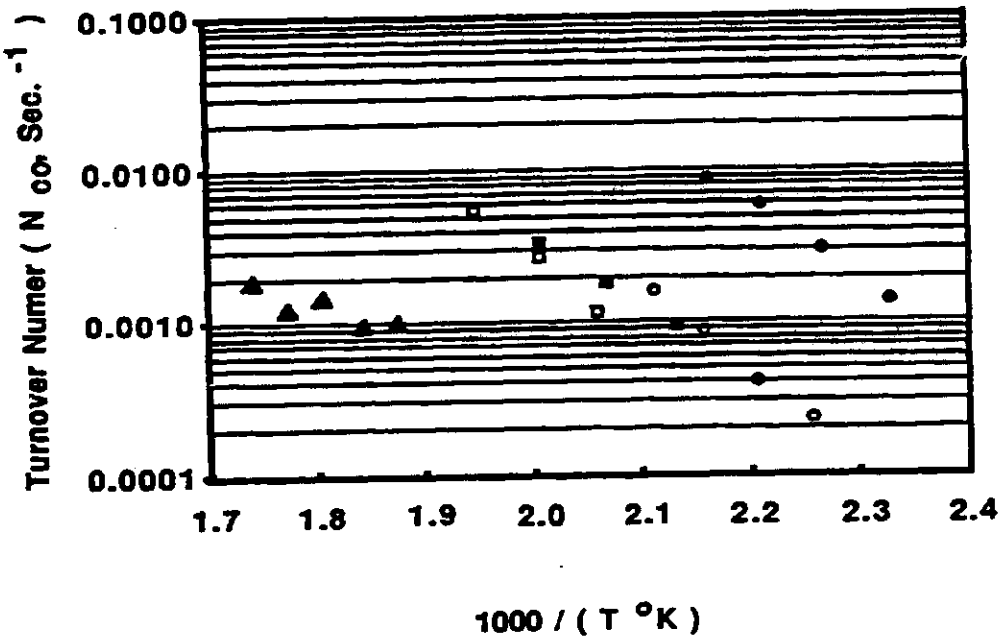

Figure 18. Arrhenius Plot for Unsupported borided cobalt catalysts.
P = 1 atm, H_2 / CO = 2.
● CoB-250, ○ CoB/Na-250, ■ Co, □ CoB-109G, ▲ Co/Na

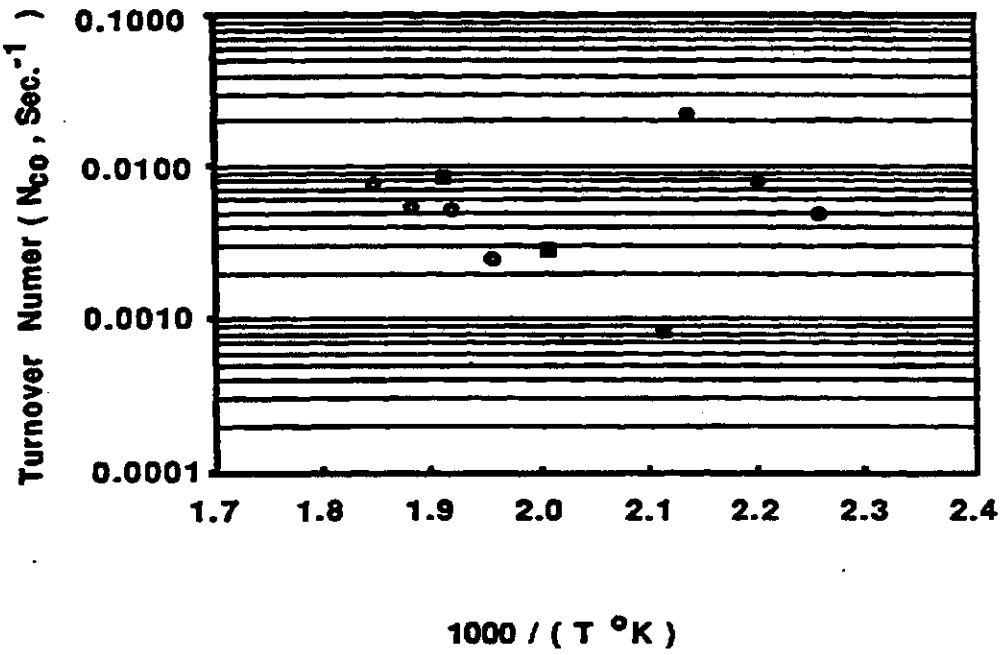

Figure 19. Arrhenius Plot for Alumina-supported borided cobalt catalysts, P = 1 atm, H_2 / CO = 2.
● CoB/Alumina-250, ● CoB/Na/Alumina-250
■ 3% Co/Alumina

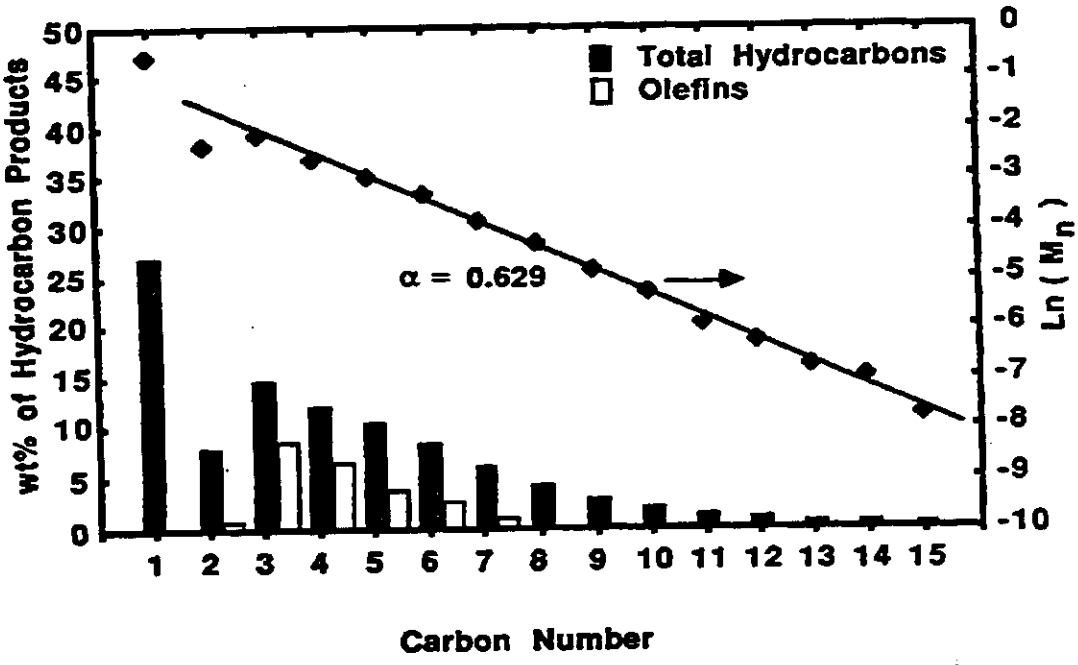

Figure 20. Hydrocarbon Product Distribution and Anderson-Schulz-Flory Plot for Co; 1atm, 210 °C, $H_2/CO = 2$, $N_{co} = 1.81 \times 10^{-3}\ Sec^{-1}$

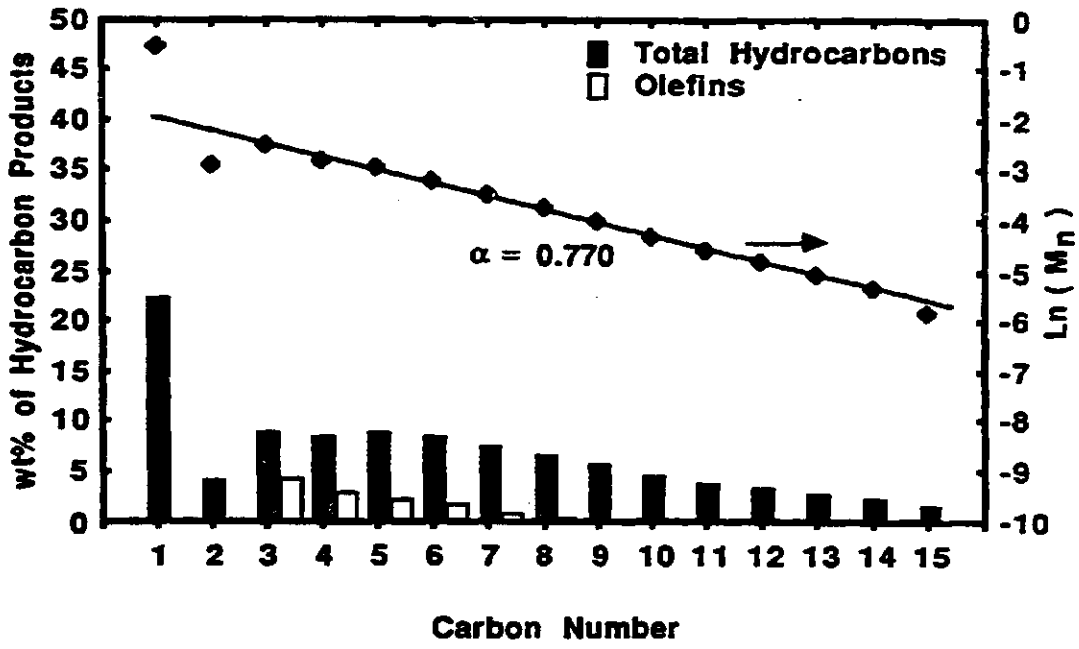

Figure 21. Hydrocarbon Product Distribution and Anderson-Schulz-Flory Plot for CoB-250; 1atm, 168 ^{o}C, $H_2/CO = 2$, $N_{co} = 3.00 \times 10^{-3}$ Sec^{-1}.

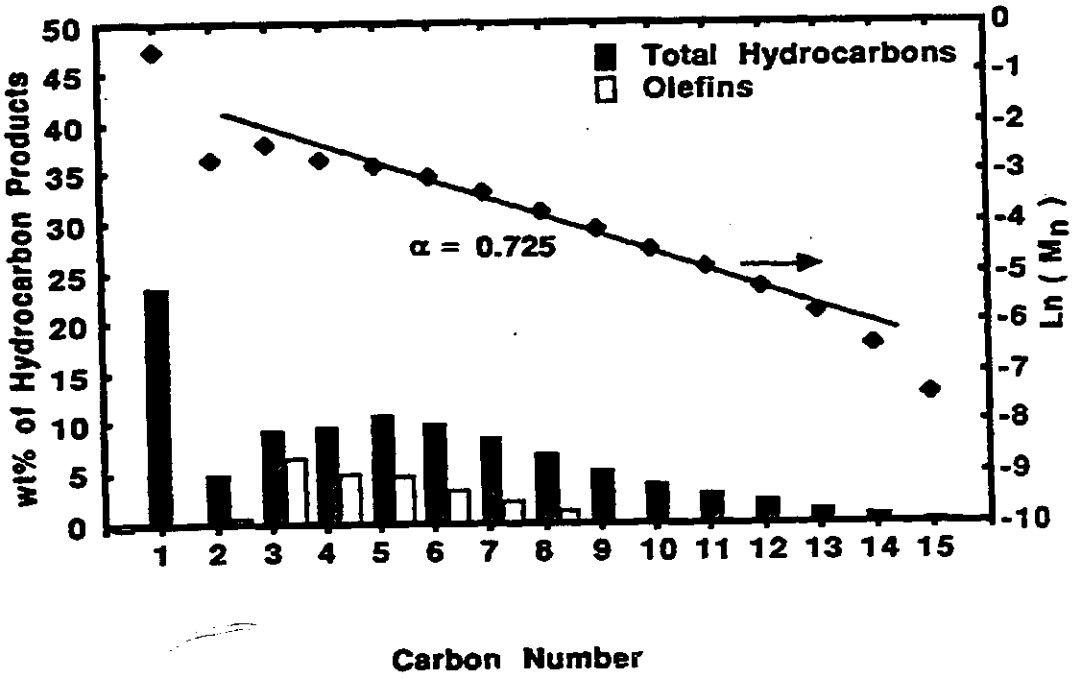

Figure 22. Hydrocarbon Product Distribution and Anderson-Schulz-Flory Plot for CoB/Na-250; 1atm, 200 °C, $H_2/CO = 2$, $N_{co} = 1.62 \times 10^{-3}\ Sec^{-1}$.