pressure and an order of -0.1 for the carbon monoxide partial pressure.

APPENDIX B

IRON-MANGANESE CATALYST COMPOSITION

The compositions of the coprecipitated iron-manganese catalysts were determined by atomic absorption spectroscopy. The spectrophotometer was a Model 351 manufactured by Instrumentation Laboratory Inc. The iron and manganese hollow cathode lamps that gave sharp emission lines used in this spectrophotometer were made by Westinghouse Electric Inc. Standard iron and manganese solutions were purchased from the J. T. Baker Chemicals Company to calibrate the instrument.

Standard iron and manganese solutions containing 0.5, 1, 2, and 4 ppm of metal were prepared for each determination. Sample solutions were prepared with the addition of heat and hydrochloric acid to dissolve all the catalyst powder. The concentration of metal in this initial solution was 1000 ppm. The sample solution was then diluted to lower concentrations until the measured metal concentration (iron or manganese) was in the range between 0.5 to 4 ppm. A comparison of the absorption intensity readings for the standard solutions and the sample solution indicates the composition of the iron-manganese catalyst. The following calculations illustrate the method used for the determination of the catalyst iron to manganese ratio. The calibration of the instrument with the prepared standard solutions gave the following results:

Standard Iron Concentration a, (ppm)	Absorption Intensity M	Standard Manganese Concentration b, (ppm)	Absorption Intensity N
0.5	0.015	0.5	0.048
1.0	0.029	1.0	0.096
2.0	0.070	2.0	0.196
4.0	0.138	4.0	0.382

These data can be correlated as follows, however; the constants apply only to the data reported in the foregoing set of data.

For iron, M = 0.0356 a - 0.0038; and for manganese, N = 0.095 b + 0.0015.

A 2 ppm iron-manganese catalyst solution tested for the iron absorption and showed a reading of 0.043. Using the linear correlation equatin for iron standard solutions obtained from the calculation in the previous page, the actual iron content in this 2 ppm catalyst solution was calculated as

$$a = (0.043 + 0.0038)/0.0356 = 1.3135 \text{ (ppm)} .$$

For a 100 ppm catalyst solution, the iron content was

$$1.3135 \times (100/2) = 65.6738 \text{ (ppm)} .$$

The manganese content in the catalyst solution could be calculated by the same method. Because the manganese content in the catalyst was much lower than the iron concentration, a 100 ppm catalyst solution was tested for the manganese absorption. The manganese absorption reading of the 100 ppm catalyst solution shown on the digital display was 0.115. Using the linear correlation equation for manganese absorption, the actual manganese content in a 100 ppm catalyst solution was calculated as:

$$b = (0.115 - 0.0015)/0.095 = 1.194 \text{ (ppm)} .$$

The manganese to iron ratio of this catalyst could be calculated as 1.194:65.6738 = 1.82 : 100.

APPENDIX E

HYDROGENATION OF CARBON MONOXIDE

BLANK REACTOR EXPERIMENTS

The determination of the activity and selectivity of the iron/manganese catalyst system over a wide range of temperatures and pressures in a stainless steel reactor system required that the activity of the reactor itself be determined. Furthermore, the catalytic activity of the catalyst bed diluent, Denstone 57, and the reactivity of the heat transfer medium were determined in the absence of the catalyst.

The conversion of carbon monoxide in a blank reactor as a function of reactor temperature at a reactor pressure of 3450 KPa is presented in Table E-1. No significant change in carbon monoxide conversion was observed as the reactor temperature increased from 297 K to 628 K. The fraction of carbon monoxide converted at 628 K and 3450 KPa was only 0.0018. The only hydrocarbon product detected in the effluent stream was methane.

The conversion of carbon monoxide in a reactor loaded with acid washed Denstone 57 particles as a function of reactor temperature is presented in Table E-2. No significant change in carbon monoxide conversion was observed as the reactor temperature increased from 442 K to 573 K, however, the conversion was slightly higher than that observed for the blank reactor without the Denstone 57. This increase in conversion is attributed to the increased surface area due to the presence of the Denstone 57 in the reactor. The fraction of carbon monoxide converted at 573 K was 0.0021 and was considered insignificant relative to the conversions attained in the presence of the iron/manganese catalysts. Once again, the only hydrocarbon product detected was methane. The conversion was approximately 33 percent higher at 623 K, however, relative to the conversion in the presence of

Table E-1

Carbon Monoxide Conversion

Blank Reactor

Total Pressure:	3450 KPa
H_2/CO Ratio:	2/1
Reactant Flow Rate:	10 cm^3s^{-1}

Reactor Temperature K	Carbon Monoxide Conversion Mole Percent
297	0.195
423	0.216
448	0.162
483	0.163
532	0.167
583	0.158
628	0.178

Table E-2

Carbon Monoxide Conversion

Denstone 57 Diluent

Total Pressure: 3450 KPa

H_2/CO Ratio: 2/1

Reactant Flow Rate: 10 $cm^3 s^{-1}$

Reactor Temperature K	Carbon Monoxide Conversion Mole Percent
442	0.209
463	0.205
489	0.195
503	0.200
538	0.202
573	0.209
628	0.284

the catalyst, it was still insignificant. At 623 K ethane and carbon dioxide were detected in the effleunt stream in addition to methane. This observation led to a definition of an upper limit on the reactor temperature as a process variables, that is, 573 K. Thus it was concluded that neither the reactor nor the catalyst bed diluent, Denstone 57, would contribute significantly to the conversion of carbon monoxide at temperatures and pressures studied in this investigation.

The heat transfer liquids used in this investigation, Mobil #1 base stock MCP-151 and n-hexadecane, were passed through the Denstone 57 loaded reactor at a flow rate of 0.103 cm^3s^{-1} in the presence of hydrogen and carbon monoxide. The operating variables in these experiments were: a reactor temperature of 543 K; total reactor pressure of 3450 KPa; a hydrogen to carbon monoxide ratio of 2/1 and a reactant gas flow rate of 10 cm^3s^{-1}. The carbon monoxide conversions at these conditions were 0.214% and 0.238% for the MCP-151 and the n-hexadecane, respectively.

The heat transfer liquids were also passed through the blank reactor at reaction temperatures and pressure to determine the extent of thermal decomposition/cracking. No hydrocarbon products were detected in the effluent stream during these experiments.

APPENDIX F

SCHULZ-FLORY DISTRIBUTION LAW

DATA AND SAMPLE CALCULATION

The application of a polymerization mechanism to explain the hydrogenation of carbon monoxide was first proposed by Anderson;[1] however, wide acceptance of this mechanism was not obtained until 1976.[73] The Schulz-Flory weight distribution law can be derived as follows: For a typical polymerization reaction, it is assumed that the value of the chain growth probability, α, is a constant, then,

$$\phi_p = \alpha^q \phi_{p-q}$$

where ϕ_p is the number of product C_p and p is greater than q. Therefore, if q = p - 1, the above equation can be written as

$$\phi_p = \alpha^{p-1} \phi_1 .$$

The weight fraction of C_p can be represented as follows:

$$m_p = p\phi_p / \left(\sum_{p=1}^{\infty} p\phi_p\right)$$

$$= p\phi_1 \alpha^{p-1} / \left(\sum_{p=1}^{\infty} p\phi_1 \alpha^{p-1}\right)$$

$$= p\alpha^{p-1} / \left(\sum_{p=1}^{\infty} p\alpha^{p-1}\right)$$

$$= p\alpha^{p-1} / (1 + 2\alpha + 3\alpha^2 + \cdots)$$

$$= p\alpha^{p-1} / \frac{\partial}{\partial \alpha}(\alpha + \alpha^2 + \alpha^3 + \cdots)$$

$$= p\alpha^{p-1} / [\frac{\partial}{\partial \alpha}(\sum_{p=0}^{\infty} \alpha^p)]$$

$$= p\alpha^{p-1} / [\frac{\partial}{\partial \alpha}(1 - \alpha)^{-1}]$$

$$= p\alpha^{p-1} (1 - \alpha)^2 .$$

For α greater than 0.5, this equation can be written as:[73]

$$m_p = p(\ln_e{}^2 \alpha)\ \alpha^p$$

or

$$\log_{10}(m_p/p) = p \log_{10}\alpha + \log_{10}(\ln_e{}^2 \alpha) .$$

Plot $\log_{10}(m_p/p)$ versus p, a straight line, can be obtained with a slope of $\log_{10}\alpha$. The value of α can be calculated from both the slope and intercept.

A special series of experiments were conducted to test the Schulz-Flory distribution law for the hydrogenation of carbon monxide in the diluted-bed reactor with the iron/manganese catalysts. The reaction conditions were: reaction temperatures 518 K and 533 K; pressure = 3450 KPa; H_2/CO = 2/1; and space velocity = 1 $cm^3g^{-1}s^{-1}$. Each experiment lasted for a period of eight hours. Several gas samples were taken during the course of the experiment and analyzed by gas chromatograph as described in Chapter 3. Usually the carbon monoxide conversions and hydrocarbon product selectivities varied in a range of

5 percent. The arithmatic average of these analyses was assumed to be typical of the composition of the product gas in this calculation. The absolute weight of each component in the gas sample was calculated as shown in Table F-1. Room temperature and pressure of the laboratory were 298.15 K and 87.65 KPa, respectively. The liquid hydrocarbon product collected in the condenser during the eight hours of the experiment was 1.16671 grams. The average flow rate of gas stream at the exit of the system was 6.832 cm^3s^{-1}. The total output gas volume during eight hours was 6.832 x 3600 x 8 = 196761.6 cm^3. The weight of the liquid hydrocarbon product collected in the condenser corresponding to one cm^3 of gas sample was 1.16671/196761.6 = 5.9296×10^{-6} grams. The composition of liquid hydrocarbon product was analyzed in the series 5730A Hewlett Packard gas chromatograph as described in Chapter 3. The weight percent of each component in the liquid hydrocarbon product is presented in Table F-2. The FID response factors for all hydrocarbons were assumed to be unity in this calculation. The assumption was based on a recent report by Dietz[98] who investigated FID response factors for hydrocarbons and found the values are all approximately 1.0 except benzene and toluene. The value of the $\log_{10}(m_p/p)$ for each carbon number at a reaction temperature of 518 K is listed in Table F-3. Figure 28 was plotted from the data in Table F-3. The value of the $\log_{10}(m_p/p)$ for each carbon number at a reaction temperature of 533 K is listed in Table F-4. Figure 29 was plotted from the data in Table F-4.

Table F-1

Gaseous Hydrocarbon Product Analysis

Diluted-Bed Reactor

Temperature = 533 K; Pressure = 3450 KPa;

H_2/CO = 2/1; Space Velocity = 1.08 $cm^3 g^{-1} s^{-1}$

Component	Partial Volume Percentage Gas Sample	Molecular Weight ($g\ mol^{-1}$)	Absolute Weight* in 1 cm^3 Gas Sample
CH_4	1.1067	16	6.2552×10^{-6}
C_2H_4	0.3037	28	3.0040×10^{-6}
C_2H_6	0.2940	30	3.1157×10^{-6}
C_3H_6	0.4047	42	6.0045×10^{-6}
C_3H_8	0.1293	44	2.0098×10^{-6}
$i\text{-}C_4H_{10}$	0.0092	58	1.8850×10^{-7}
$1\text{-}C_4H_8$	0.1276	56	2.5242×10^{-6}
$n\text{-}C_4H_{10}$	0.1170	58	2.3972×10^{-6}
$2\text{-}C_4H_8$	0.0671	56	1.3274×10^{-6}
C_5H_{10}	0.0963	70	2.3813×10^{-6}
C_5H_{12}	0.0733	72	1.8644×10^{-6}
C_6H_{12}	4.0410×10^{-2}	84	1.1991×10^{-6}
C_6H_{14}	3.9110×10^{-2}	86	1.1879×10^{-6}
C_7H_{14}	2.2802×10^{-2}	98	7.8960×10^{-7}
C_7H_{16}	2.1614×10^{-2}	100	7.6353×10^{-7}
C_8H_{16}	3.0816×10^{-3}	112	1.2191×10^{-7}
C_8H_{18}	8.7345×10^{-3}	114	3.5175×10^{-7}
		Total	3.5486×10^{-5}

*Absolute weight of each component in 1 cm^3 gas sample collected at 87.65 KPa and 298.15 K.

Table F-2

Liquid Hydrocarbon Product Analysis

Diluted-Bed Reactor

Temperature = 533 K; Pressure = 3450 KPa;

H_2/CO = 2/1; Space Velocity = 1.08 $cm^3 g^{-1} s^{-1}$

Carbon Number	Peak Area	Weight Percent*
7	27	2.2095
8	79	6.4648
9	139	11.3748
10	156	12.7660
11	155	12.6841
12	137	11.2111
13	113	9.2471
14	88	7.2013
15	62	5.0736
16	57	4.6645
17	48	3.9280
18	42	3.4370
19	38	3.1097
20	33	2.7005
21	25	2.0458
22	23	1.8822
Total	1222	100.0000

*For each hydrocarbon component, the response factor for the FID was assumed to be one.

Table F-3

Schulz-Flory Distribution Law Calculation

Diluted-Bed Reactor

Temperature = 518 K; Pressure = 3450 KPa;

H_2/CO = 2/1; Space Velocity = 1 $cm^3 g^{-1} s^{-1}$

Carbon Number p)	Relative Weight	Weight Fraction (m_p)	$Log_{10}(m_p/p)$
1	2.720×10^{-5}	3.096×10^{-1}	-5.092×10^{-1}
2	1.262×10^{-5}	1.437×10^{-1}	-1.144
3	1.660×10^{-5}	1.890×10^{-1}	-1.201
4	1.334×10^{-5}	1.519×10^{-1}	-1.421
5	8.460×10^{-6}	9.630×10^{-2}	-1.715
6	2.640×10^{-6}	3.005×10^{-2}	-2.300
7	1.570×10^{-6}	1.787×10^{-2}	-2.593
8	3.531×10^{-7}	4.019×10^{-3}	-3.299
9	9.364×10^{-7}	1.066×10^{-2}	-2.927
10	1.167×10^{-6}	1.328×10^{-2}	-2.877
11	9.211×10^{-7}	1.049×10^{-2}	-3.021
12	5.373×10^{-7}	6.116×10^{-3}	-3.293
13	3.377×10^{-7}	3.844×10^{-3}	-3.529
14	2.767×10^{-7}	3.150×10^{-3}	-3.648
15	1.966×10^{-7}	2.272×10^{-3}	-3.820
16	1.650×10^{-7}	1.878×10^{-3}	-3.930
17	1.420×10^{-7}	1.616×10^{-3}	-4.022
18	1.075×10^{-7}	1.224×10^{-3}	-4.168
19	8.443×10^{-8}	9.611×10^{-4}	-4.296
20	5.680×10^{-8}	6.466×10^{-4}	-4.490
21	4.298×10^{-8}	4.883×10^{-4}	-4.633
22	3.070×10^{-8}	3.495×10^{-4}	-4.799
23	2.303×10^{-8}	2.622×10^{-4}	-4.943
24	1.919×10^{-8}	2.184×10^{-4}	-5.041
25	1.689×10^{-8}	1.923×10^{-4}	-5.114

Table F-4

Schulz-Flory Distribution Law Calculation

Temperature = 533 K; Pressure = 3450 KPa;

H_2/CO = 2/1; Space Velocity = 1 $cm^3 g^{-1} s^{-1}$

Carbon Number (p)	Relative Weight (gram)	Weight Fraction (m_p)	(m_p/p)	$Log_{10}(m_p/p)$
1	6.2552×10^{-6}	1.5104×10^{-1}	1.5104×10^{-1}	-8.2092×10^{-1}
2	6.1197×10^{-6}	1.4776×10^{-1}	7.3882×10^{-2}	-1.1315
3	8.0143×10^{-6}	1.9351×10^{-1}	6.4503×10^{-2}	-1.1904
4	6.4373×10^{-6}	1.5543×10^{-1}	3.8858×10^{-2}	-1.4105
5	4.2457×10^{-6}	1.0251×10^{-1}	2.0503×10^{-2}	-1.6882
6	2.3870×10^{-6}	5.7635×10^{-2}	9.6059×10^{-3}	-2.0175
7	1.6841×10^{-6}	4.0663×10^{-2}	5.8091×10^{-3}	-2.2359
8	8.5700×10^{-7}	2.0693×10^{-2}	2.5866×10^{-3}	-2.5873
9	6.7448×10^{-7}	1.6286×10^{-2}	1.8095×10^{-3}	-2.7424
10	7.5697×10^{-7}	1.8277×10^{-2}	1.8277×10^{-3}	-2.7381
11	7.5211×10^{-7}	1.8160×10^{-2}	1.6509×10^{-3}	-2.7823
12	6.6477×10^{-7}	1.6051×10^{-2}	1.3376×10^{-3}	-2.8737
13	5.4831×10^{-7}	1.3299×10^{-2}	1.0184×10^{-3}	-2.9921
14	4.2701×10^{-7}	1.0310×10^{-2}	7.3646×10^{-4}	-3.1329
15	3.0084×10^{-7}	7.2639×10^{-3}	4.8426×10^{-4}	-3.3149
16	2.7658×10^{-7}	6.6782×10^{-3}	4.1739×10^{-4}	-3.3795
17	2.3291×10^{-7}	5.6237×10^{-3}	3.3081×10^{-4}	-3.4804
18	2.0380×10^{-7}	4.9209×10^{-3}	2.7338×10^{-4}	-3.5632
19	1.8439×10^{-7}	4.4522×10^{-3}	2.3433×10^{-4}	-3.6302
20	1.6013×10^{-7}	3.8664×10^{-3}	1.9332×10^{-4}	-3.7137
21	1.2131×10^{-7}	2.9291×10^{-3}	1.3948×10^{-4}	-3.8555
22	1.1161×10^{-7}	2.6949×10^{-3}	1.2249×10^{-4}	-3.9119

APPENDIX G

CARBON MONOXIDE HYDROGENATION OVER IRON/MANGANESE CATALYSTS: DILUTED-BED REACTOR, PROCESS VARIABLE DATA

The process variable investigation in the diluted-bed reactor included a determination of the effects of reactor temperature, reactor pressure, space velocity and hydrogen to carbon monoxide on the activity (as measured by carbon monoxide conversion), product distribution (as measured by methane, C_2-C_4 hydrocarbons, C_5^+ hydrocarbons, alcohols and carbon dioxide yields) and selectivity (as measured by the olefin to paraffin ratio of C_2-C_4 hydrocarbons). The data for the hydrogenation of carbon monoxide in the diluted bed reactor obtained in the course of this research project are presented in Tables G-1 through G-10 of this appendix.

Table G-1

Effect of Temperature on Yield and Selectivity for Carbon Monoxide Hydrogenation in the Diluted-Bed Reactor

Pressure = 2070 KPa; H_2/CO = 2/1; Space Velocity = 0.5 $cm^3 g^{-1} s^{-1}$

Activity		Product Distribution								Selectivity			
		Yields (%)								Olefin/Paraffin Ratio			
Temp. (K)	CO Conv. (%)	C_1	C_2	C_3	C_4	C_2-C_4	C_5^+	R-OH	CO_2	C_2	C_3	C_4	C_2-C_4
463	3.90	16.1	15.7	19.6	16.3	51.6	19.1	6.4	6.9	3.2	2.6	2.4	2.7
473	6.57	15.1	15.0	18.7	15.8	49.5	20.0	5.6	9.9	3.2	2.9	2.6	2.9
483	11.09	14.2	13.7	17.7	15.3	46.7	19.5	4.5	15.1	3.4	3.3	2.8	3.2