APPENDIX C

SLURRY REACTOR DESIGN STUDIES

REVIEW OF FIXED-BED AND SLURRY REACTOR KINETICS

Contents

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REVIEW OF FIXED-BED AND SLURRY REACTOR REACTION KINETICS

When trying to match observed conversions with slurry reactor model predictions (Section 2.4.3) it was found that a new expression for the kinetic constant had to be developed. It was also necessary to get an insight into the differences, if any, between slurry reactor and fixed-bed kinetics, to examine any differences between iron and cobalt catalysts and to look at pressure effects. This review is by no means complete, but some observations were made that could be useful to future investigators.

<u>Fused Magnetite Catalyst - Slurry vs Fixed-Bed</u> - Data of Satterfield, et al (IEC Fund. **24**, 450, 1985)

This data was of interest since it consisted of a direct comparison of the same catalyst in a fixed-bed reactor and in a well-mixed slurry reactor. The authors concluded that "...the catalyst activity in the fixed-bed appears to have been moderately greater than in the slurry reactor." They could not ascribe the difference to the higher inlet pressure in the fixed-bed reactor but thought the fixed-bed catalyst might have been reduced in a more optimal manner. Catalyst activity, expressed in μmols of $CO + H_2$ converted/[min · g of cat · atm of H_2], varied from 100 to 190 over the temperature range 233 to 250 °C in the fixed-bed measurements. Over approximately the same range, they observed values of 78 and 130 in the slurry reactor.

It was of interest to see whether this same data could be fit to the simplified models discussed earlier in this report. Figure C-1 shows the result of plotting the fixed-bed CO conversion data in the form indicated by the plug-flow model (Model 1). A temperature correction was applied by multiplying $GHSV^{-1}$ by an exponential activation energy term. An activation energy of 80 kJ/gmol brought the data onto one curve. Values of α of 0.0 and -0.5 were tested and, somewhat unexpectedly, a value of 0.0 gave the best straight line. The fixed-bed data were obtained on a fine catalyst diluted with inert material and placed in a reactor tube surrounded by a fluidized sand bath. GHSV is expressed in $Nm^3/(h \cdot kgCat)$.

The slurry reactor data were obtained in a small, stirred autoclave so that mass transfer resistance could be minimized. A CSTR model (Model 3) should be most applicable under these circumstances and one was developed for this project. It is presented at the end of Appendix C. Figure C-2 shows the best straight-line fit to the CO conversion data using this model, which was obtained using an activation energy of 135 kJ/gmol and an α of -0.6. It is not known why the activation energy was higher than in the fixed-bed case, but activation energies of this magnitude have been reported for the Fischer-Tropsch reaction where mass transfer effects are known to be insignificant.

<u>Cobalt Fixed-Bed Kinetics</u> - Data of Singleton and Regier (Hyd. Proc., p 71 -74, May 1983) - Data of Post, et al (AIChEJournal, 35, 1107-1114, 1988)

The fixed-bed data of Singleton and Rogier are of interest because they represent a new cobalt type catalyst, developed by Gulf before their merger with Chevron, and because a pressure effect is presented. Increased pressure is shown to increase "catalyst activity" but the effect diminishes with increasing pressure. The authors present a table of CO conversion data taken at low pressure in a 1" diameter, single tube, pilot plant in which space velocity is given per gram of catalyst. They also present 250 psig data which are apparently on a volumetric space velocity basis and can be related to their low pressure data and their reported pressure effect if a catalyst bulk density of roughly 500 kg/m^3 is assumed. The Gulf technology described in this paper was later sold to Shell.

Post, et al, present a review of diffusional effects in fixed-bed F-T catalysts which quantifies the effects of particle size and pore diameter. The catalyst is a Zirconium promoted cobalt catalyst developed by Shell, presumably to be used in their new plant in Malaysia. Some data are given for iron catalysts but not enough to quantify differences. Space velocity and STY are given per m^3 of catalyst, rather than per kg of catalyst, and on this basis there does not appear to be much difference between catalysts at comparable particle size.

Figure C-3 presents a correlation of the Shell data on H_2 conversion and Gulf data on CO conversion using a Model 1 (plug flow) type plot. The value of α used is that reported by Post, et al. To compare Figures C-1 and C-3, multiply the ordinate in C-3 by the expected catalyst density in kg/m^3. If, for example, this density is 500, then a coordinate value of 2 on Figure C-3 corresponds to a coordinate value of 4 on Figure C-1. On this basis, conversions are roughly comparable. Figure C-1 mixes H_2 and CO Conversions, which is unfortunate, but can't be helped. It can be stated, however, that with 2.0 H_2/CO ratio feed gas and a catalyst with low water gas shift activity, the two conversions should be of comparable magnitude.

The ARGE design point (precipitated iron catalyst) and the design point selected for this study are also indicated in Figure C-1. It would be of value to have a better definition of space velocity requirement and the pressure effect for various catalysts, but it is felt that the design point represents a reasonable concensus of the above information for a "generic" catalyst..

Table C-1 compares the various kinetic curve fits developed in this report over the temperature range of interest. Columns 2 and 3 represent Figures C-1 and C-2, respectively. Column 4 is the Gulf correlation line from Figure C-3, assuming a catalyst bulk density of 532 kg/m^3, and column 5 is the ARGE design point. Column 6 represents the equation developed to fit the Rheinprussen laboratory data[5] in Section 2 and is expressed in terms of hydrogen conversion:

$$k'_H = k_H / (kgCat/m^3) = 3.3\cdot 10^9 \cdot e^{(-130,000/RT)}$$

The slurry concentration and gas holdup correspond to estimated Rheinprussen laboratory conditions.

[5] The comparable expression given by Deckwer was expressed in terms of wt% Fe:

$$k'_H = k_H / \text{wt \% Fe} = 112,000 \cdot e^{(-70,000/RT)}$$

CSTR MODEL FOR FISCHER-TROPSCH

Model 3

Assumptions: Basically the same assumptions as for Model 1 and Model 2, except that both gas phase and liquid phase are fully mixed so that the concentrations in the reactor - both phases at steady state - are those corresponding to the product gas composition. Other assumptions:

1. Only gas/liquid mass transfer and the reaction terms are important, liquid/solid mass transfer is negligible.
2. Intraparticle diffusion is negligible.
3. First order reaction rate, $r = k_r \cdot \varepsilon_L \cdot C_H$.
4. Constant usage ratio, U, (moles of CO consumed per mole of H_2 consumed).
5. Stoichiometry handled by means of a contraction factor, α, which is constant.
6. Liquid phase batch (liquid flow can be neglected).
7. Catalyst is uniformly dispersed.
8. Reaction rate expressed in terms of catalyst loading:
   $k_r = k_H = k'_H \cdot (\text{kgCat/m}^3)$ where $k'_H = 3.3 \cdot 10^9 \cdot e^{(-130{,}000/RT)} \cdot (P/1100)^{0.5}$, T in ^oK, P in kPa, k_r in $\sec^{-1}$ (Section 2.4.3).
9. k_La and ε_G are established at an average value of superficial velocity u_G.
10. The correction to k_La for solids content, previously derived, applies.

$$Q^o \cdot C^o_{HG} - Q \cdot C_{HG} = k_La \cdot (C^*_{HL} - C_{HL}) \cdot V_L = k_r \cdot \varepsilon_L \cdot C_{HL} \cdot V_L$$

$He/RT = H_H = C_{HG}/C^*_{HL}$, where He is Henry's law constant.

By definition of the contraction terms, α and $\alpha^* = \alpha \cdot (1 + U)/(1 + I)$:

$$Q = Q^o \cdot (1 + \alpha^* \cdot X_H)$$

$$Q^o \cdot C^o_{HG} \cdot X_H = Q^o \cdot C^o_{HG} - Q \cdot C_{HG} = Q^o \cdot C^o_{HG} - Q^o \cdot (1 + \alpha^* \cdot X_H) \cdot C_{HG}$$

$$C_{HG} = C^o_{HG} \cdot (1 - X_H) / (1 + \alpha^* \cdot X_H)$$

$$k_La \cdot (C_{HG}/H_H - C_{HL}) = k_r \cdot \varepsilon_L \cdot C_{HL}$$

$$C_{HL} = k_La \cdot C_{HG}/H_H / (k_r \cdot \varepsilon_L + k_La)$$

$$(Q^o/V_L)\cdot C^o_{HG}\cdot X_H = ((k_r\cdot \varepsilon_L\cdot k_L a)/(k_r\cdot \varepsilon_L + k_L a))\cdot C_{HG}/H_H$$

$$\text{Let } K_L a = (k_r\cdot \varepsilon_L\cdot k_L a)/(k_r\cdot \varepsilon_L + k_L a)$$

$$(Q^o/V_L)\cdot C^o_{HG}\cdot X_H = (K_L a/H_H)\cdot C_{HG} = (K_L a/H_H)\cdot C^o_{HG}\cdot(1 - X_H) / (1+ \alpha^*\cdot X_H)$$

$$X_H\cdot(1+ \alpha^*\cdot X_H)/(1 - X_H) = (K_L a/H_H)\cdot V_L/Q^o = K_L a\cdot R\cdot T\cdot L/(He\cdot u^o_G) = \text{Stanton No.}$$

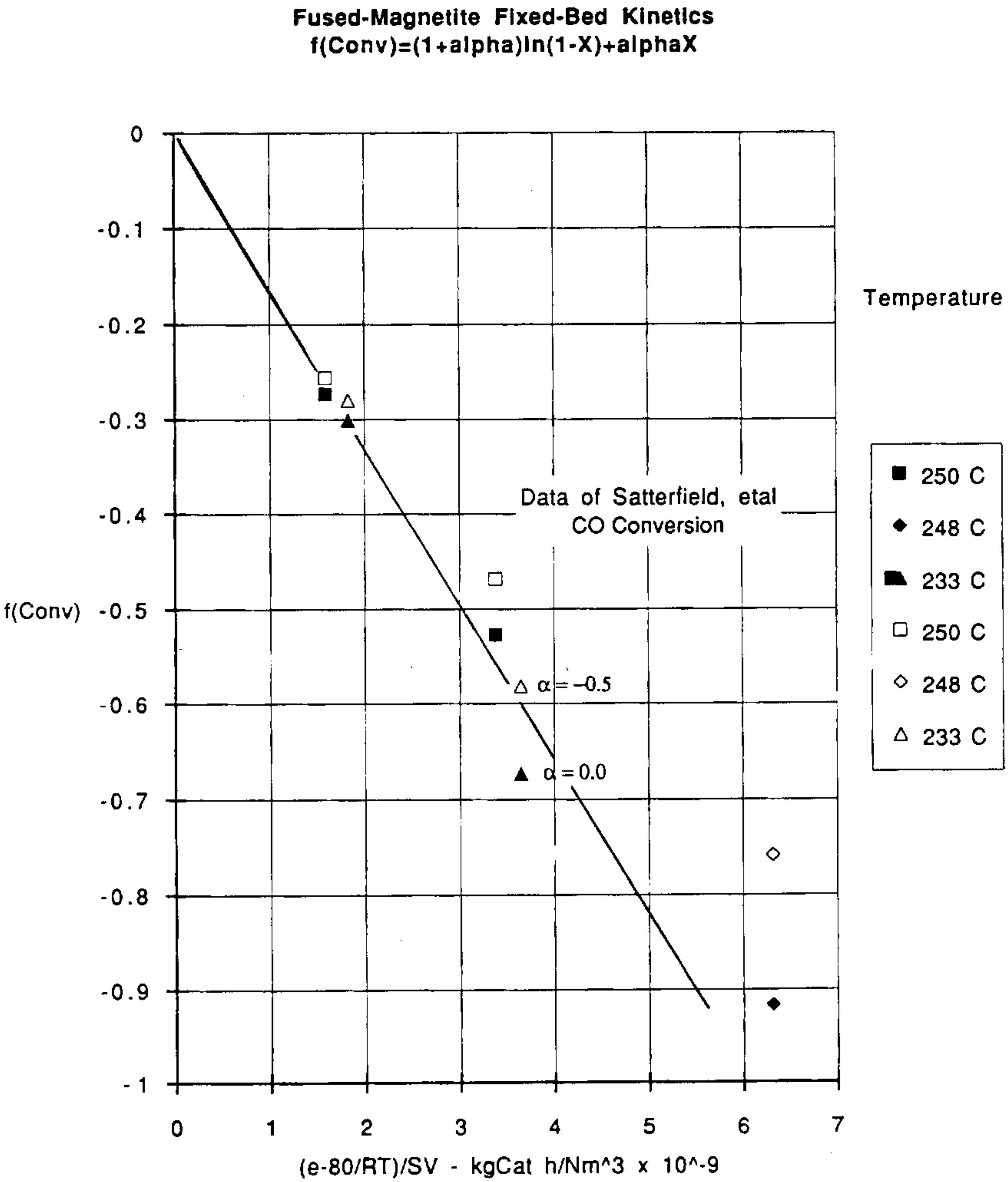
For $\alpha^* = -0.5$

X_H	Stanton No.
0.95	9.975
0.90	4.95
0.80	2.40

For $\alpha^* = 0.0$

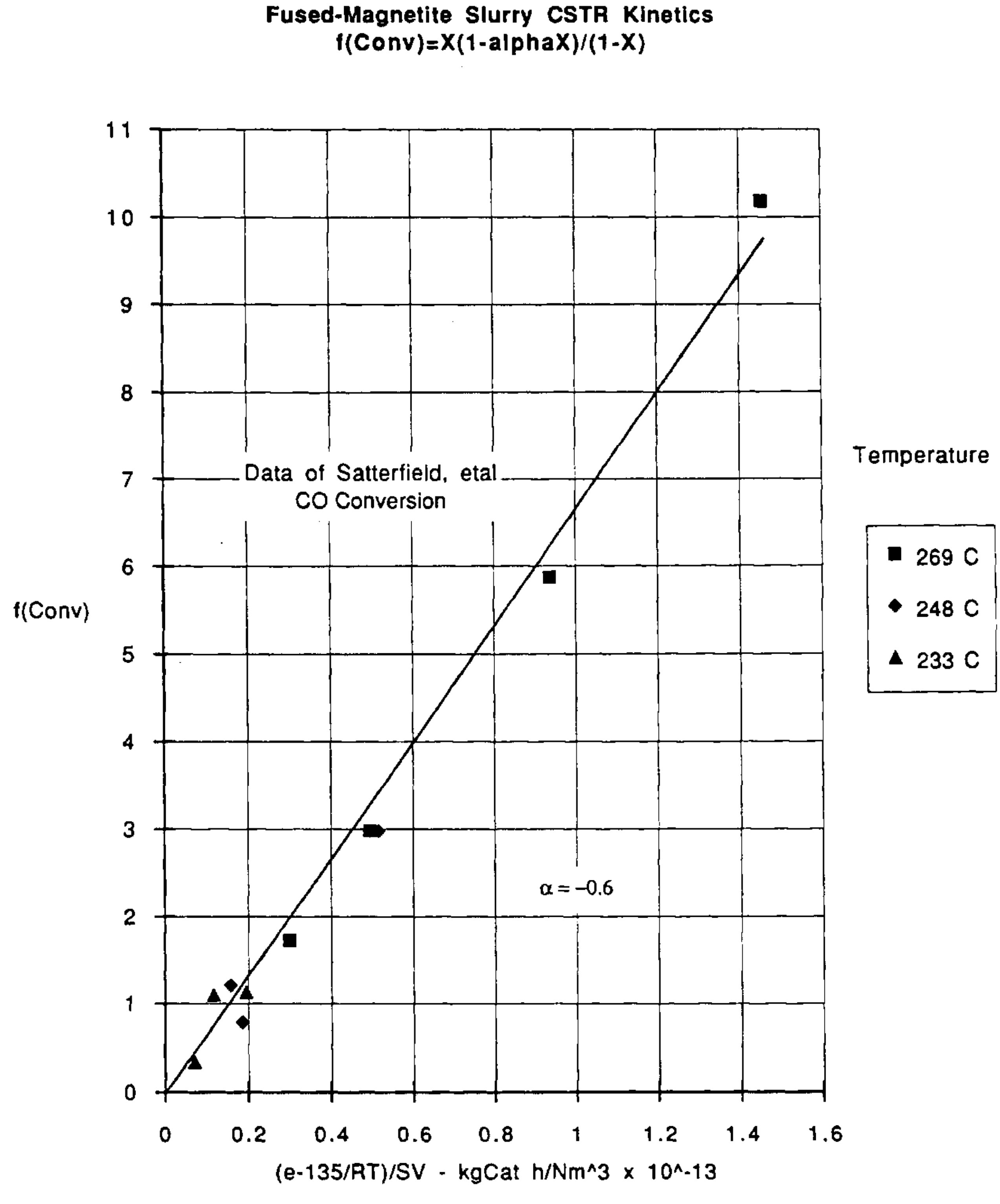
X_H	Stanton No.
0.95	19.0
0.90	9.0
0.80	4.0

Figure C-1



Fused-Magnetite Fixed-Bed Kinetics
f(Conv)=(1+alpha)ln(1-X)+alphaX
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1
f(Conv)
0
1
2
3
4
5
6
7
(e-80/RT)/SV - kgCat h/Nm^3 x 10^-9
Data of Satterfield, etal
CO Conversion
α = –0.5
α = 0.0
Temperature
250 C
248 C
233 C
250 C
248 C
233 C

Figure C-2



Fused-Magnetite Slurry CSTR Kinetics
f(Conv)=X(1-alphaX)/(1-X)
11
10
9
8
7
6
5
4
3
2
1
0
f(Conv)
Data of Satterfield, etal
CO Conversion
α = -0.6
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
(e-135/RT)/SV - kgCat h/Nm^3 x 10^-13
Temperature
269 C
248 C
233 C

Figure C-3

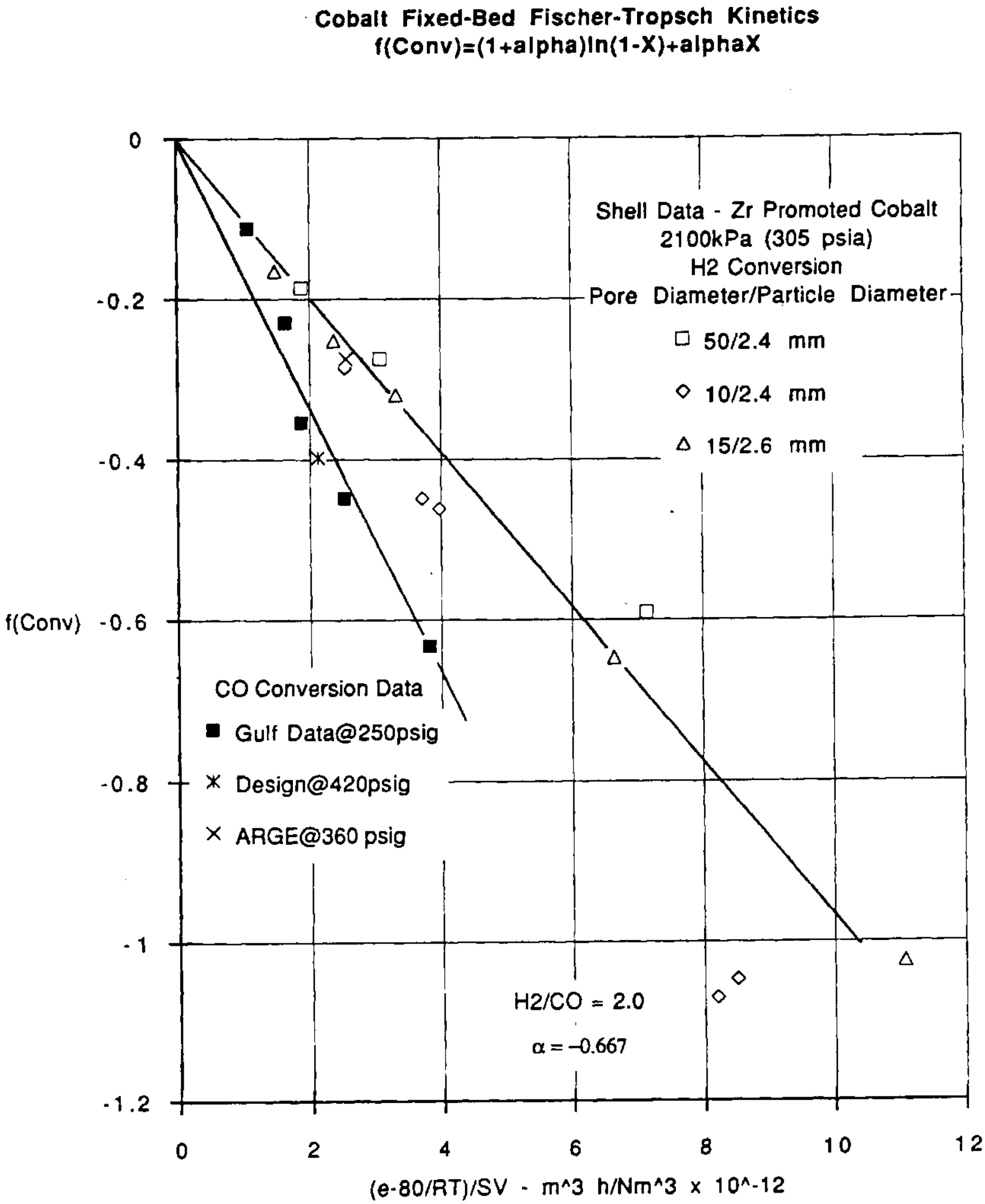

Cobalt Fixed-Bed Fischer-Tropsch Kinetics
f(Conv)=(1+alpha)ln(1-X)+alphaX
Shell Data - Zr Promoted Cobalt
2100kPa (305 psia)
H2 Conversion
Pore Diameter/Particle Diameter
50/2.4 mm
10/2.4 mm
15/2.6 mm
CO Conversion Data
Gulf Data@250psig
Design@420psig
ARGE@360 psig
H2/CO = 2.0
α = -0.667
f(Conv)
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
0
2
4
6
8
10
12
(e-80/RT)/SV - m^3 h/Nm^3 x 10^-12

Table C-1

	1	2	3	4	5	6	7
1		CO Conversion Data				H2 Conversion	
2		Fe Fixed-Bed	Fe Slurry	Co Fixed-Bed	ARGE	Slurry Model	4/18/90
3	Source	Satterfield, et.al. (1983)		Singleton (1983)	ECT Ed.2, Vol.4.	Used for Design	
4	Pressure-atm	8.88	7.8	18	25.5	10.86	
5	T - oC	Rate Constant in Nm3 H2+CO Conv/(h KgCat) [same as NL/(h gCat)]					Comments
6	200	0.23398579	0.08250512	0.438723357	0.273470893	0.056214709	Divide by 0.7
7	210	0.35653921	0.16794022	0.668511022	0.416705204	0.114333656	to convert to
8	220	0.53407779	0.33212859	1.001395849	0.624203413	0.225938446	Nm3/(h kgFe)
9	230	0.78727001	0.63926718	1.476131273	0.920121827	0.434554363	
10	240	1.14307034	1.1994213	2.143256879	1.335963454	0.814749051	Mult. by 3.6/.7
11	250	1.63617258	2.19689992	3.067823597	1.912276709	1.49129862	to convert to
12	260	2.31068508	3.93356363	4.332534525	2.700613187	2.668418441	cm3/(s gFe)
13	270	3.22203906	6.89357292	6.041323239	3.765758152	3.716685987	
14	Preexponential	1.6x10^8	6.69x10^13	3.0x10^8	1.87x10^8		
15	Act. Energy kJ/m	80	135	80	80		
16							
17	T - oC	Rate Constant in millimols H2+CO Conv/(m KgCat atm)					
18	200	35.4361994	14.2251521	32.77848444	14.42253315	6.96130652	Nm3/(h kgCat)
19	210	53.9964182	28.9554775	49.94668686	21.97654222	14.15842297	times
20	220	80.8839156	57.2640791	74.81762189	32.91975363	27.97891892	22.4*60/atm.
21	230	119.228852	110.219496	110.2866878	48.52614265	53.81271545	
22	240	173.113368	206.798685	160.1298656	70.45714086	100.8938411	
23	250	247.791705	378.779344	229.207327	100.8512239	184.6738524	
24	260	349.943888	678.206886	323.6980961	142.4271623	330.4416073	
25	270	487.964753	1188.55803	451.3673969	198.6016546	460.2530371	
26							
27	T - oC	Rate Constant in Nm3/(h m3)					
28	200	198.887922	8.19837714	233.4008261	232.4502589	5.585948853	Nm3/(h kgCat)
29	210	303.05833	16.5610914	355.6478639	354.1994234	11.27478655	times
30	220	453.966118	32.5012641	532.7425918	530.5729008	22.10976484	Catalyst Density
31	230	669.17951	62.0737804	785.3018372	782.1035527	42.19586595	kg/m3
32	240	971.609785	115.558248	1140.212659	1135.568936	78.49699935	line 33 or
33	250	1390.7467	209.997441	1632.082153	1625.435202	142.5503689	E40 thru E47
34	260	1964.08232	373.022565	2304.908367	2295.521209	253.0479697	
35	270	2738.7332	650.588117	3213.983963	3200.894429	350.7661073	
36	Bulk Density	850		532	850		
37	Fract Voids	0.37		0.37	0.37	Slurry Model Used for Design	
38	Part. Dens.	1349.20635	3100	844.4444444	1349.206349	(no mass transfer resistance)	
39	% Slurry		15	Rheinprussen Lab Unit Condition		Preexponential	3300000000
40	Gas Holdup		0.1664	"	"	Act. Energy	130
41	T - oC		Liq Dens.	Slurry Dens.	Kg Cat/m3	ko	koxEpsilonL
42	200		702.5	794.6905077	99.36810108	0.00172998	0.001442112
43	210		696.95	788.6517548	98.61301542	0.003403846	0.002837446
44	220		691.4	782.6093307	97.85747071	0.006513473	0.005429631
45	230		685.85	776.5632319	97.10146652	0.01214194	0.010121521
46	240		680.3	770.5134552	96.34500244	0.022083047	0.018408428
47	250		674.75	764.4599972	95.58807805	0.03924075	0.032711089
48	260		669.2	758.4028544	94.83069292	0.06821642	0.056865207
49	266		665.87	754.7667988	94.37604052	0.094108054	0.078448474
50							
51	T - oC	Rate Constant in s^-1				Hh = He/RT	koEpsilL/Hh
52	200	0.01077932	0.00050586	0.006240593	0.004387184	5.825534097	0.00024755
53	210	0.0167724	0.00104346	0.009710234	0.006826367	5.561181682	0.000510224
54	220	0.02564438	0.0020902	0.014846589	0.010437264	5.316602872	0.001021259
55	230	0.03856848	0.00407302	0.02232888	0.015697371	5.08982521	0.001988579
56	240	0.05711249	0.00773319	0.033064775	0.023244785	4.879117343	0.003772901
57	250	0.08334348	0.01432702	0.04825097	0.033920795	4.682954546	0.006985139
58	260	0.11995236	0.02593597	0.069445358	0.048820609	4.499989848	0.012636741
59	266	0.16914547	0.04574411	0.097925279	0.068842207	4.396043873	0.017845244