CONVERSION AND SELECTIVITY CALCULATIONS

CALCULATIONS USE ON LINE GAS ANALYSES

C = CONCENTRATION IN MOLE %

CONVERSIONS

$$\text{CONVERSION (CO)} = \frac{\left(\frac{C_{co}}{C_{Ar}}\right)_{Feed} - \left(\frac{C_{co}}{C_{Ar}}\right)_{Prod}}{\left(\frac{C_{co}}{C_{Ar}}\right)_{Feed}}$$

$$\text{CONVERSION (H}_2) = \frac{\left(\frac{C_{H_2}}{C_{Ar}}\right)_{Feed} - \left(\frac{C_{H_2}}{C_{Ar}}\right)_{Prod}}{\left(\frac{C_{H_2}}{C_{Ar}}\right)_{Feed}}$$

$$\text{CONVERSION (CO + H}_2) = \frac{\left(\frac{C_{co} + C_{H_2}}{C_{Ar}}\right)_{Feed} - \left(\frac{C_{co} + C_{H_2}}{C_{Ar}}\right)_{Prod}}{\left(\frac{C_{co} + C_{H_2}}{C_{Ar}}\right)_{Feed}}$$

SELECTIVITIES

$$S_a = \frac{\left(\dfrac{C_A}{C_{Ar}}\right)_{Prod}}{\left(\dfrac{C_{Co}}{C_{Ar}}\right)_{Feed} - \left(\dfrac{C_{Co}}{C_{Ar}}\right)_{Prod}}$$

The equation above yields carbon-based selectivities. Before being used the selectivities were corrected for carbon dioxide formation in all cases except for that of carbon dioxide itself. Since carbon dioxide selectivities were usually about 50%, the corrected selectivities were about twice as high as they would have been if the carbon going to carbon dioxide had been taken into account in their calculation.

CALCULATION OF CONTACT TIME

$$F_0 \ (moles/hr) \rightarrow \boxed{\infty} \rightarrow F \ (moles/hr)$$

$\overline{V}$ is volume of liquid in Autoclave

W is weight in grams of Iron

material balance:

$$F_0 - F = \overline{r} \cdot W \cdot \overline{V}$$

$$F_0 - F_0 (1-x) = \overline{r} \cdot W \cdot \overline{V}$$

$$F_0 x = \overline{r} \cdot W \cdot \overline{V}$$

$$\overline{r} = \frac{F_0 \cdot x}{W \overline{V}} = \frac{x}{\left(\frac{W\overline{V}}{F_0}\right)}$$

$$\frac{W\overline{V}}{F_0} = \text{CONTACT TIME (SPACE TIME)}$$

246

APPENDIX 2

NONLINEAR REGRESSION OF THE FISCHER-TROPSCH
PRODUCT DISTRIBUTION BY A DOUBLE α MODEL

THE SINGLE α MODEL

Classical Shulz-Flory theory states that the hydrocarbon product of the Fischer-Tropsch process can be described by the equation:

$$M_n = (1-\alpha) \alpha^{(n-1)} \qquad (1)$$

where M_n is the mole fraction of the product of carbon number n, and α is the chain growth probability, defined as

$$\alpha = \frac{r_p}{r_p + r_t} \qquad (2)$$

where r_p and r_t are the rate of propagation and termination, respectively.

Equation (1) is called a single α model since it describes the product distribution over the entire range of carbon number by a single parameter α. From Equation (1) one gets

$$Ln(M_n) = nLn\alpha + Ln\frac{1-\alpha}{\alpha} \qquad (3)$$

Equation (3) tells that this single α model generates a straight line in a $Ln(M_n)$-n plot, and the slop of the line will be the log of α.

DEVELOPMENT OF DOUBLE α MODELS

The single α model has been successfully applied to, for example, the product on a fused iron catalyst (Satterfield and Huff, 1982). However, a break point was observed in many cases which separates the distribution into two regions. This phenomenon was first found in 1943 by tests conducted in Germany, and more and more similar cases were reported since then (Huff and Satterfield, 1984; Donnely et al, 1988). As a consequence, the single α model has been modified to account for the two region distributions. The simplest way to do this is using the single α model in each region and thus two straight lines result, each giving an α for the specific region (Huff and Satterfield, 1984; Madon and Taylon, 1981). Based on experimental observations, Huff (Huff, 1982) proposed a two-site theory, which assumes that two kinds of sites on the surface of the catalyst exit, one in favor of producing lighter products and the other heavier products. When the products produced at these two kinds of sites do not interact, and assume that x percent of the total moles of the products are produced at site 1, the total product is then the sum of products from the two sites:

$$M_n = x(1-\alpha_1)\alpha_1^{n-1} + (1-x)(1-\alpha_2)\alpha_2^{n-1} \qquad (4)$$

Equation (4) contains three parameters. In addition to x, α_1 and α_2 are the chain growth probabilities at the two sites, respectively. Unlike the regional fitting by the single α model, this model actually presents a continuous, smoothly changing curve in a $Ln(M_n)$-n plot. This is better than the two separated straight lines because in many cases the two regions are not very well separated at a specific carbon number, instead, there is usually a transient region over several carbon numbers, and therefore the double α model of Equation (4) can use more data points and fit the data better (Bukur et al, 1990). When the number of the data available for evaluation of α_1 by linear (single α) model is limited, this nonlinear feature of the double α model becomes an important advantage. For this reason, the fitting of the model to the experimental data can be termed nonlinear regression.

The two-site theory is basically a pure hypothesis, and it seems difficult to argue that only two kinds of sites exit. Stenger (Stenger, 1985) tried to attack the problem by making a more realistic assumption that the chain growth probability α changes continuously over the range of carbon numbers. Based on the idea, Stenger proposed a distributed-site model. He assumed that α is a function of the local potassium concentration c, and c obeys the normal distribution. Stenger's model is also a three-parameter model and he showed that the distributed-α model and the

two-site model fit experimental data equally well, but the calculation procedure is more involved with the former because numerical integration is required. The differences between the two models are also discussed by Inoue et al (Inoue et al, 1987).

Recently Donnelly et al (Donnelly et al, 1988) proposed a double α model in the form

$$M_n = A\alpha_1^{n-1} + B\alpha_2^{n-1} \qquad (5)$$

The two parameters A and B are functions of the two α's and a third variable called the "break point" ξ, which is the carbon number at which the curve turns. The expressions of A and B can be found as follows. At the break point $n=\xi$, the contributions from each term in Equation (5) are equal, therefore we have

$$A\alpha_1^{\xi-1} = B\alpha_2^{\xi-1}$$

or

$$B = \left(\frac{\alpha_1}{\alpha_2}\right)^{\xi-1} A \qquad (6)$$

A second relation between A and B can be derived by noticing that the sum of the mole fraction of all carbon numbers is unity:

250

$$\sum_{n=1}^{\infty} M_n = \sum_{n=1}^{\infty} (A\alpha_1^{n-1} + B\alpha_2^{n-1}) = 1 \qquad (7)$$

Using the sum of the geometric series

$$\sum_{n=1}^{\infty} y^{n-1} = \frac{1}{1-y}$$

we get from Equation (7)

$$\frac{A}{1-\alpha_1} + \frac{B}{1-\alpha_2} = 1 \qquad (8)$$

Equations (6) and (8) are linearly independent and can be used to evaluate A and B explicitly when the parameters α_1, α_2 and ξ are chosen. Therefore the model given by Equation (5) is also a three parameter model which is similar to Huff's (Huff, 1982). Actually, if Equation (5) is compared with Equation (4), it can be seen that the two equations are identical if we set

$$A = x(1-\alpha_1)$$

and

$$B = (1-x)(1-\alpha_2)$$

and the break point ξ plays a similar role as x. However, Donnelly et al emphasize that the model given by Equation (5) is not based on any theoretical assumptions about the cause of the double α phenomenon, instead, it is a mathematical tool to provide a tractable measure of evaluating α's by fitting the experimental data. The nonlinear regression method associated with this model is by choosing α_1, α_2 and ξ to minimize the sum of the squared errors:

$$\phi = \sum_{n=1}^{k} [Ln(M_n) - Ln(m_n)]^2 \qquad (9)$$

where M_n is calculated mole fraction of product of carbon number n by Equation (5), and m_n is actually measured mole fraction. The sum is taken from 1 to k, with k being the highest carbon number where reliable data are available.

MODELS USING WEIGHT FRACTIONS

In many cases the product distribution is more conveniently expressed by weight fraction rather than the mole fraction. Assume that during the chain growth, the molecular weight of each additional carbon unit is the same, the single α model corresponding to Equation (1) is given as (Satterfield et al,

1982):

$$W_n = n(1-\alpha)^2 \alpha^{n-1} \qquad (10)$$

where W_n is the weight fraction of the product of carbon number n.
Similarly to the development of the double α model of Equation (5)
we propose a weight fraction distribution:

$$\frac{W_n}{n} = C_1 \alpha_1^{n-1} + C_2 \alpha_2^{n-1} \qquad (11)$$

The two relations giving C_1 and C_2 are given, in this case, by

$$C_2 = \left(\frac{\alpha_1}{\alpha_2}\right)^{\xi-1} C_1 \qquad (12)$$

and

$$\sum_{n=1}^{\infty} W_n = \sum_{n=1}^{\infty} (C_1 n \alpha_1^{n-1} + C_2 n \alpha_2^{n-1}) = 1 \qquad (13)$$

The binomial series relation gives

$$\sum_{n=1}^{\infty} n y^{n-1} = \frac{1}{(1-y)^2}$$

Therefore the second relation between C_1 and C_2 is

253

$$\frac{C_1}{(1-\alpha_1)^2} + \frac{C_2}{(1-\alpha_2)^2} = 1 \qquad (14)$$

The nonlinear regression is done by choosing α_1, α_2 and ξ to minimize the sum of the squared errors:

$$\Delta = \sum_{n=1}^{k} [Ln(W_n) - Ln(w_n)]^2$$

where W_n and w_n are the weight fractions calculated from Equation (11) and from the experimental data, respectively.

REFERENCES

Bukur, D. B., Mukesh, D. and Patel, S. A., "Promoter Effects on Precipitated Iron Catalysts for Fischer-Tropsch Synthesis", *Ind. Eng. Chem. Res.*, 29, 194-204, 1990

Donnelly, T. J., Yates, I. C. and Satterfield, C. N., "Analysis and Prediction of Product Distributions of the Fischer-Tropsch Synthesis", *Energy & Fuel*, 2, 734-739, 1988

Huff, G. A., Jr. and Satterfield, C. N., "Evidence for Two Chain Growth Probabilities on Iron Catalysts in the Fischer-Tropsch Synthesis", *J. Catalyst*, 85, 370-379, 1984

Huff, G. A., Jr., "Fischer-Tropsch Synthesis in a Slurry Reactor", Sc. D. Thesis, Massachusetts Institute of Technology, 1982

Inoue, M., Miyake, T. and Inui, T., "Simple Criteria to Differentiate a Two-Site Model from a Distributed-Site Model for Fischer-Tropsch Synthesis", *J. Catalyst*, 105, 266-269, 1987

Madon, R. J. and Taylor, W. P., "Fischer-Tropsch Synthesis on a Precipitated Iron Catalyst", *J. Catalyst*, 69, 32-43, 1981

Satterfield, C. N. and Huff, G. A., Jr., "Carbon Number Distribution of Fischer-Tropsch Products Formed on an Iron Catalyst in a Slurry Reactor", *J. Catalyst*, 73, 187-197, 1982

Stenger, H. G., Jr., "Distributed Chain Growth Probabilities for the Fischer-Tropsch Synthesis", *J. Catalyst*, 92, 426-426, 1985

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APPENDIX 3

Date: 3 NOV 93
From: Alan E. van Til & Ronald S. Smyczynski
To: George J. Antos

Subject: Fischer-Tropsch (1C834-0016), #17

This month, three additional TGA carbide synthesis runs were made since the last report to you. We first heated ca. 200 mg of material to nominally 200 °C in a 1-torr vacuum to remove the two waters of hydration from the K,Cu,Fe oxalate. Then, the material was further heated to 250 °C in H_2 at atmospheric pressure to remove the remaining carbonaceous species and form doped Fe(0). The temperature was purposely kept below or near 300 °C to avoid sintering since all previous work via TGA and scaleup showed loss of surface area above 300 °C.[1] Although it may not be necessary in commercial practice of this synthetic pathway, we wanted to bring the doped Fe catalyst to a definite thermodynamic starting point, that of full reduction to Fe(0) before cutting in CO or CO/H_2; therefore, we normally used H_2 to fully reduce the iron. The first run made this month, RUN #14, also used 2:1 H_2:CO as was done earlier in RUN's 7-12. The second run, #15, had to be aborted due to the thermalbalance lifting mechanism jamming. Three weeks later after finally finding the true problem, we finally finished this series with RUN #16, where the H_2:CO ratio was set nominally at 1. The thermalbalance, a Mettler TA-2 is 22 years old, therefore, Mettler does not support it with spare parts any longer. Also, the level of repair done by us here of total disassembly was originally done under service contract and accordingly we have no manuals explaining how to do such work. The primary results from the present runs are that increased H_2 improves CO conversion dramatically and after about 10 HOS produces more wax as seen in Figure 1. In contrast of earlier runs carried out at 300 °C, the wax formation on the sample & sample stick continued with little change for 100+ hrs. Samples of the product gases were taken in RUN's 14 & 16. The results are not consistent throughout as we would like because of sampling problems inherent to the use of sample tubes. However, they do provide very useful information. Namely, at 250 °C in contrast to the earlier results of RUN #11 at 300 °C, with 2:1 H_2:CO, we are producing C2 & C3's. We would not know that fact without gas analysis. Also, CO_2 is being produced throughout RUN #14 but not in RUN #16 where it stopped after 20+ hrs. Little or no methane was produced over this catalyst at 250 °C when the H_2:CO ratio=1. In summary, from our work using a thermalbalance microreactor for F-T and butene isomerization, we suggest that a GC be found to hook to analyze product gases on-line to produce more consistent results. Finally, the techniques shown here where the catalyst mass is continuously monitored should provide the means of evaluating ideas on how to reduce wax buildup which fundamentally limits catalyst performance. Much shorter run times of about 24-hrs should be sufficient for this purpose.

Figures 2-6 summarize our microreactor run data. The bulk thermoanalytical data for each run are given in Table 1. Table 2 lists our gas sample results taken during RUN #11. Using the usual method of calculating conversions from the mole ratio of species to N_2, we obtain Table 3. Similiarly, Tables 4-7 list the present gas analysis results for RUN's 14 & 16. From the data accumulated to date, the recommended procedure for scaleup of our F-T iron carbide catalyst is as follows:

(1) Use a stirred autoclave without supporting liquid.
(2) Heat doped iron oxalate to 200 oC while stirring slowly under rotary pump vacuum at 1-2 torr collecting water evolved in trap(s). Continue heating until no more water is evolved and as a check that water collected mass balances with the two waters of hydration.
(3) Bring autoclave back to atmospheric pressure with N_2, then cut in N_2 and heat to 250 oC. Use a CO or CO_2 monitor connected to the autoclave outlet to tell when we have removed the initial carbonaceous species from the iron. Continue heating until we reach near zero lineout, and then cut in CO and raise pressure to about 50 psig. Hold temperature for 6-8 hrs and finally cool down under H_2 + CO to RT. Cut reaction gases and sparge with N_2. Finally, cut pressure and stirring.

REFERENCES: (1) UOP RESEARCH REPORT 42-3-17U, A.E. van Til,
March, 1993
(2) UOP B# 6753:126,128,130

CC: SABRADLEY,RFRAME,MJCOHN,TMMEZZA

TABLE 1
THERMOANALYTICAL DATA FOR DOPED Fe_2C_y FROM Fe,Cu,K OXALATE BY VACUUM, H_2, AND CO OR CO/H_2 TREATMENT AT 250 or 300 °C

RUN #	ms,i(mg) (a.b.)	ms,f(mg) (a.b.)	% Mass Loss (a.b.)	% Mass Loss (t.b.)	Rx Gas P(psia)	BET S.A. (m²/g)
1 CO	218.05	95.73	56.10	61.84	CO (14.7)	
2	202.07	81.68	59.58	59.95	CO (14.7)	
3	199.86	82.54	58.70	60.95	CO (14.7)	37
4	201.90	142.64	29.35	34.35	CO (65)	
5	206.12	75.75	63.63	61.93	CO/H_2=1 (14.7)	13
6	202.91	87.39	56.93	59.93	CO/H_2=1 (65)	52
7	202.03	94.97	52.99	53.85	CO/H_2=2 (65)	19
8	209.79	117.61	43.94	38.97	CO/H_2=2 (65)	
9	212.26	110.11	48.12	41.16	CO/H_2=2 (65)	
10 VAC	202.50	124.94	38.30	29.58	CO/H_2=2 (65)	
11	202.58	126.00	37.80	28.02	CO/H_2=2 (65)	
12 250°C	199.36	128.89	35.35	25.63	CO/H_2=2 (65)	
13	200.28	82.26	58.93	59.27	CO/H_2=2 (14.7, 65)	
14 250°C	206.34	157.42	23.71	0.77	CO/H_2=2 (65)	
15	204.67	RUN	ABORTED			
16 250°C	208.44	160.29	23.10	4.75	CO/H_2=1 (65)	

259

NOTES:
1) RUN #1 prep and carbiding done entirely in CO after vacuum treatment at 1-torr up to and holding to mass lineout at 200 °C. Balance was backfilled with UHP N2 before cutting in CO over the sample.
2) RUN #10 sample prep done entirely in vacuum to 300 °C rather than stopping at 200 °C, backfilling with UHP N2 to atmospheric pressure and cutting in H2 over the sample and continuing the heating to 300 °C(RUN's 2-9).
3) RUN #11 was a repeat of RUN's 7-9 conditions and gas samples were also taken.
4) RUN #12 prep was done using H2 sweep at 250 °C. After mass lineout, CO was cut in and the temperature was held at 250 °C for 84+hrs.
5) RUN #14, Total HOS with CO=94.5
6) RUN #16, Total HOS with CO=117

TABLE 2

GAS SAMPLE RESULTS FROM RUN #11, TGA F-T CARBIDE SYNTHESIS

TIME (HOS)	CO Mol %	CO2 Mol %	H2 Mol %	CH4 Mol %	N2 Mol %
0.25	3.5	1.0	35.1		59.7
6.0	9.5	0.6	26.4	0.2	62.5
24.0	12.4	0.3	29.8	0.3	56.7
31.0	10.3	0.1	24.6	0.2	64.4
49.5 Reactor Cooled	12.2		31.4		56.1

TABLE 3

CONVERSION AND SELECTIVITY DATA FOR RUN #11 FROM GC ANALYSIS

TIME HOS	CO Percent Conversion	H2/CO	CO2 Percent Selectivity	CH4 Percent Selectivity
0.25	73.0	10.0	10.5	
6.0	30.1	2.78	14.7	4.9
24.0		2.40		
31.0	26.5	2.36	2.7	5.6

TABLE 4

GAS SAMPLE RESULTS FROM RUN #14, TGA F-T CARBIDE SYNTHESIS

TIME (HOS)	CO Mol %	CO₂ Mol %	H₂ Mol %	CH₄ Mol %	SUM(C2+C3) Mol %	N₂ Mol %
0.25	1.5	0.4	8.2			89.5
4	4.6	0.7	19.0	0.1		75.1
12	17.0	3.3	47.6	0.6	0.4	30.6
20	10.0	1.7	22.5	0.4	0.1	54.4
30	10.1	1.0	32.4	0.2		56.2
40	11.8	1.4	35.6	0.3	0.2	50.5
50	13.0	1.0	38.8	0.2		46.9
72	9.2	1.0	29.9	0.2		59.6
94.25	10.1	1.0	32.0	0.2		56.6
After Cool Down	12.0	0.1	31.5			56.3

TABLE 5

CONVERSION AND SELECTIVITY DATA FOR RUN #14 FROM GC ANALYSIS

TIME (HOS)	CO % Conv.	H₂/CO	CO₂ % Sel.	CH₄ % Sel.	C2+C3 % Sel.
0.25	92.1	5.44	2.3		
4	71.3	4.12	6.1	0.9	
12		2.8			
20	13.8	2.25	107	25	6.9
30	15.7	3.21	53	11	
40		3.03			
50		2.89			
72	27.6	3.25	29	5.7	
94.25	16.3	3.17	51	10	

261

TABLE 6

GAS SAMPLE RESULTS FROM RUN #16. TGA F-T CARBIDE SYNTHESIS

TIME (HOS)	CO Mol %	CO2 Mol %	H2 Mol %	N2 Mol %
0.25	2.6	0.1	4.0	93.0
4	4.2	0.2	6.5	88.8
12	8.5	0.2	11.9	79.0
20	9.5	0.2	13.6	76.4
30	Sampling	Problem		
40	0.1		1.0	79.5
50	8.3		11.7	79.6
72	Sampling	Problem		
94.25	7.8		11.2	80.7
116.75	7.7		11.1	80.8
After Cooldown	7.8		11.3	80.6

TABLE 7

CONVERSION AND SELECTIVITY DATA FOR RUN #16 FROM GC ANALYSIS

TIME (HOS)	CO % Conversion	H2/CO	CO2 % Selectivity
0.25	71.1	1.54	1.5
4	51.1	1.55	4.6
12		1.40	
20		1.43	
30			
40			
50		1.41	
72			
94.25	0.1	1.43	
116.75	1.5	1.44	
After Cooldown		1.45	

TGA Prep: Fe₃Cu₁.₅ Carbide from Oxalate

TGA Prep: $Fe_3Cu_{1.5}$ Carbide from Oxalate

Run # 14 H2CO - 2

Run # 16, H2CO - 1

Average Sample Temperature during Carbiding
Reaction = 258 C
CO flow/g sample for RUN #14 = 539 cc/g, start,
RUN #16 = 473 cc/g, start

Time (hr)
H2/CO = 1,2

Mass Gain/Loss (%)

TGA Prep: Fe₃Cu₁C Carbide from Oxalate

TGA Prep: Fe₃C(?) Carbide from Oxalate

Temperature (C)

Time (hr)

265

TGA Prep FeCuO₄ Carbide from Oxalate

266

TGA Prep:Fe3Ct: Carbide from Oxalate

Time (hr)

Mass Gain/Loss (%)

T.A Pure Fe₃O₄/Fe Oxide from Oxalate

268

TGA Prep:Fe₃Cu₁ Carbide from Oxalate

Mass Gain/Loss (%)

Time (hr)

269
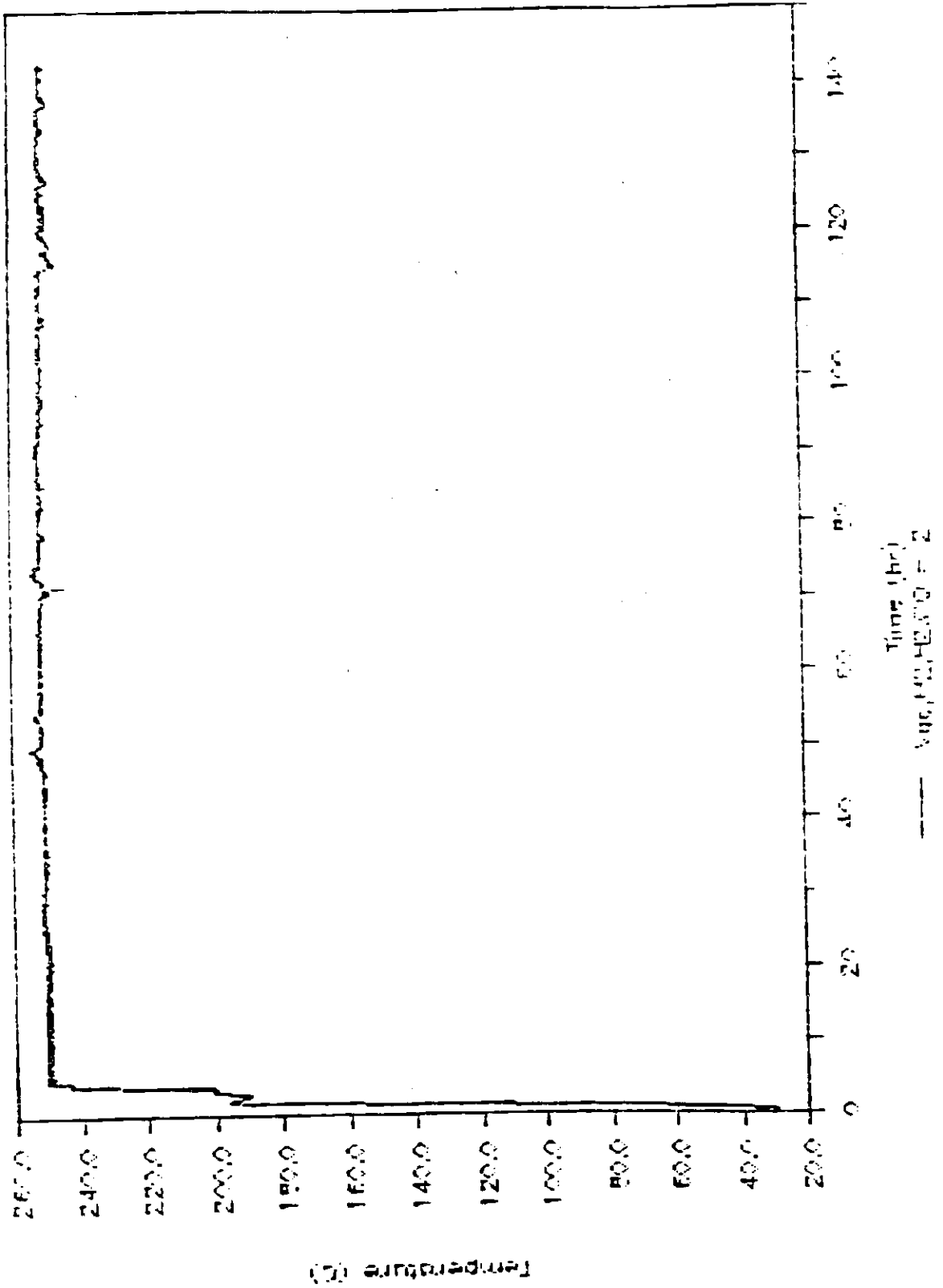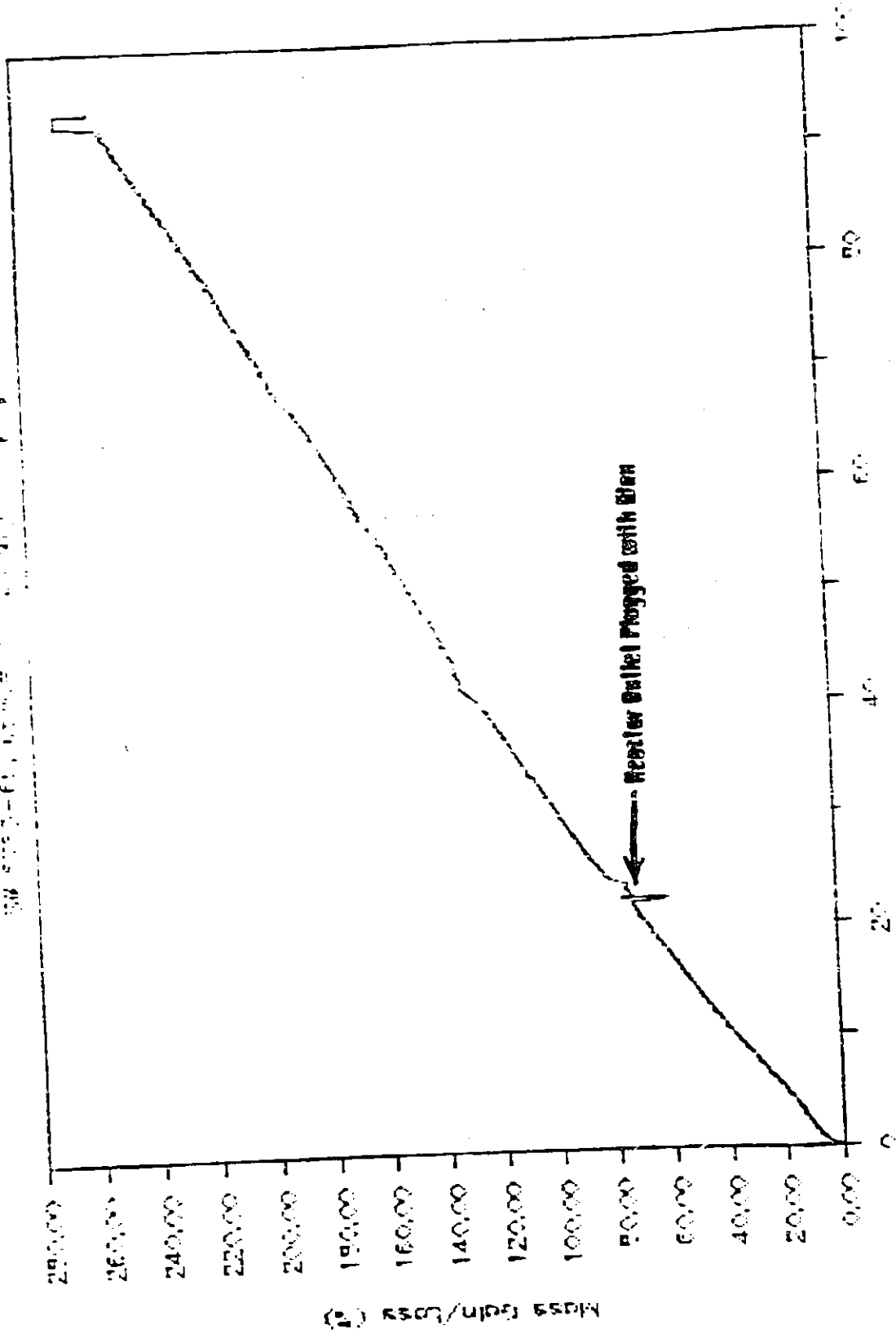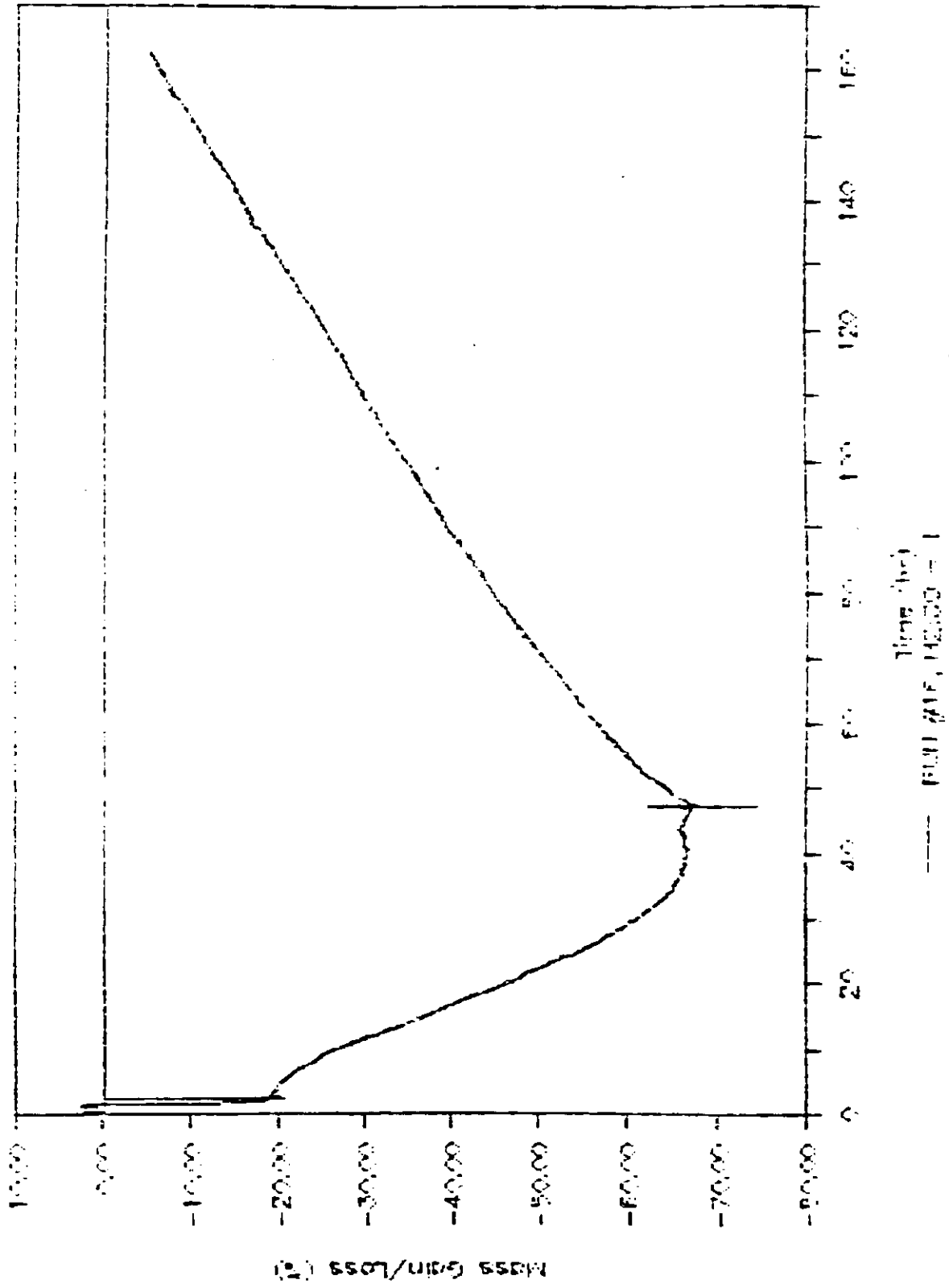
APPENDIX 4

Lewis Liu used the data set below from Run 43, Plant 700B (or 701) to calculate a rate constant. Run 43 was the second run with potassium laurate. He used a rate expression based on earlier literature work, references to which are attached. The data set is on the following pages:

Hours on Stream	Feed Rate Q_{CO+H_2}[1]	$(Q_{CO+H_2})^{-1}$	X_{H_2}[2]	U[3]	$f(X_{H_2})$[4]
15-152	2.4	.417	55	.56	.846
152-220	1.2	.833	70	.57	1.419
222-240	3.8	.263	43	.58	.573
240-246	5.2	.192	31	.61	.371
246-296	1.2	.833	73	.58	1.598
296-326	6.7	.149	29	.57	.342

1. $NL/hr \cdot g\ Fe$

2. Conversion

3. H_2/CO Usage Ratio

4. $f(X_{H_2})$ from the following:

$$\frac{(1 + \frac{1}{U}) X_{H_2} (1 + \alpha^* X_{H_2})}{1 - X_{H_2}} = Da$$

$$\alpha^* = \alpha \frac{1 + \frac{1}{U}}{1 + \frac{1}{F}} = \alpha \frac{1 + \frac{1}{U}}{1 + \frac{1}{.7}} \Rightarrow F = \text{feed ratio} = 0.7$$
$$(H_2 : CO\ \text{ratio})$$

let $\alpha = -0.5$ $U \approx .578$ $\therefore \alpha^* = -.56$

$$\text{let } \frac{(1 - 0.56 X_{H_2}) X_{H_2}}{1 - X_{H_2}} = f(X_{H_2})$$

(α is gas volume reduction due to conversion)

$$D_a = \frac{K \cdot M_{cat} \cdot R_T}{H_{H_2} \cdot Q^0 \cdot C_{H_2}}$$
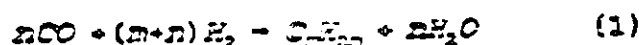
$K =$ This is a Constant (Reaction Rate Parameter) if the

reaction is first order in dissolved hydrogen.

Reaction is usually first order in H_2.

$M_{cat} =$ mass of iron

CSTR MODEL OF SLURRY REACTORS FOR
FISCHER-TROPSCH SYNTHESIS

STOICHIOMETRY (Ledakowicz, et al, 1985)

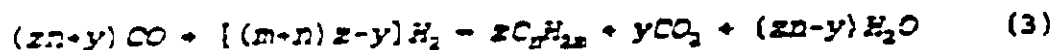Fischer-Tropsch

$$nCO + (m+n)H_2 \rightarrow C_nH_{2m} + nH_2O \qquad (1)$$

Water Gas Shift (WGS)

$$CO + H_2O = H_2 + CO_2 \qquad (2)$$

Overall Reaction

$$(zn+y)CO + [(m+n)z-y]H_2 \rightarrow zC_nH_{2m} + yCO_2 + (zn-y)H_2O \qquad (3)$$

Where z = C_nH_m produced by reaction (1), mole;
   y = H_2O produced by WGS, mole.

SELECTION OF A KINETIC MODEL

Available Kinetic Models

Deckwer et al (1986) have given a good summary of the kinetic models of the Fischer-Tropsch Synthesis (FTS) in the slurry phase. The common features of these models are:
   (1) The conversion rate of H_2, CO is directly proportional to the hydrogen concentration in the slurry;   *e.g. Assumption: zero order in CO_2;*
   (2) The effect of CO is considered.   *usual assumption in lit. as well*
The main difference is which of the inhibition effects by CO_2 or H_2O is included.

$(CO_2?)$

273

Accordingly, they can be summarized into three groups:

(A) "H₂O only". This model was proposed by Satterfield and co-workers and verified by experimental data with reduced fused magnetite catalyst (Huff and Satterfield, 1984a; Yates and Satterfield, 1989). Using a method of deliberate addition of H₂O in the synthesis gas feed, Deckwer et al (1986) also confirmed the correlation. This model is given as (Deckwer et al, 1986):

$$-r_{CO+H_2} = \frac{b_1 C_{H_2}}{1 + b_2 (C_{H_2O}/C_{H_2} C_{CO})} \tag{4}$$

This model considers the inhibition of the reaction rate due to the competitive chemisorption of the H₂O on the catalyst surface. This is valid when a less strong WGS promoting catalyst is used and the CO conversion is high, because under such conditions the product will contain relatively large portion of water and its effect may become predominant.

(B) "CO₂ only". This model was proposed by Deckwer and co-workers and verified by experimental data with Potassium-promoted Iron catalyst (Ledakowicz et al, 1985; Deckwer et al, 1986). This model is given as (Deckwer et al, 1986):

$$-r_{CO+H_2} = \frac{b_1 C_{H_2}}{1 + b_2 (C_{CO_2}/C_{CO})} \tag{5}$$

This model includes the rate inhibition by the chemisorption of CO₂. This is the case when a highly WGS promoting catalyst is used and the CO conversion is (low,) because in this case the water produced by the F-T reaction is converted

probably means "high"

274

almost completely to CO_2 and the effect of this product in increased.

(C) "H_2O plus CO_2". Considering that different kinetics may be caused by the relative importance of H_2O and CO_2 in the product, as indicated above, it is a nature extension that some investigators tried to propose a "more complete" kinetic law which includes the inhibition effect by both H_2O and CO_2 (Ledakowicz et al, 1985; Nettelhoff et al, 1985). Unfortunately, the verification of this law is unsatisfactory (Deckwer et al, 1985). The form of this law is

$$-r_{CO-H_2} = \frac{b_1 C_{H_2}}{1 + b_2 (C_{CO_2}/C_{CO}) + b_3 (C_{H_2O}/C_{CO})} \qquad (6)$$

A modified form of this model was used by Yates and Satterfield (1989) to correlate experimental data and the results are still not encouraging. The correlation they used is

$$-r_{CO-H_2} = \frac{b_1 C_{H_2}}{1 + b_2 (C_{CO_2}/C_{CO}) + b_3 (C_{H_2O}/C_{CO}C_{H_2})} \qquad (7)$$

Finally, it should be pointed out that in some cases, a simple first order reaction rate is possible, which can be treated as a simplified case of Equation (4) when the inhibition term of water is neglected:

$$-r_{CO-H_2} = b_1 C_{H_2} \qquad (6)$$

This may be the case when CO conversion is low and the H_2/CO inlet ratio is low (Huff and Satterfield, 1984).

From the above discussions we know that which kinetic model should be used depends on the catalyst type, the operation conditions such as H_2/CO inlet ratio and conversions, and can only be determined by a test using ones own experimental data.

Test of Kinetic Models

One convenient way to test a kinetic model using experimental data is to plot the data in a proper form so one can see if the data correlates the variables in the way the model suggests. For example, Equation (4) can be rearranged in the form

$$\frac{C_{H_2}}{-r_{CO-H_2}} = \frac{1}{b_1} + \frac{b_2}{b_1}\frac{C_{H_2O}}{C_{CO}C_{H_2}} \qquad (9)$$

Since the parameters b_1 and b_2 depend on in general the catalyst used and temperature, therefore if data with the same catalyst and temperature falls on a straight line in a $C_{H_2}/(-r_{CO})$ vs. $C_{H_2O}/(C_{CO}C_{H_2})$ plot, Model A is confirmed.

Henry's Constant

In the kinetic models we need the concentrations in slurry phase, but what can be calculated first from the experimental data are usually the partial pressures in the product. The relation between the concentration and the partial

276

pressure of a specific species is given by the Henry's law:

$$P_i = H_i C_i \qquad (10)$$

Where H_i is the Henry's constant for species i. Mettelhoff et al (1985) discussed the Henry's constant for Fischer-Tropsch in the slurry phase, and gave the expression of it in the form

$$H_i = a_i \exp\left(\frac{d_i}{T}\right) \qquad (11)$$

Where the parameters a's and d's are given for H_2, CO, CO_2 and H_2O.

Calculation of the Partial Pressures

Huff and Satterfield (1984b) showed the method of calculating the partial pressure by product mean value of m and n and conversions. The equations to be used are:

$$P_{H_2} = \frac{P[F - (m+n) z + y]}{F + 1 + (1 - m - n) z} \qquad (12)$$

$$P_{CO} = \frac{P(1 - 2z - y)}{F + 1 + (1 - m - n) z} \qquad (13)$$

$$P_{CO_2} = \frac{Py}{F + 1 + (1 - m - n)z} \qquad (14)$$

$$P_{H_2O} = \frac{P(zn - y)}{F + 1 + (1 - m - n)z} \qquad (15)$$

Where z and y can be calculated by the relations

$$z = \frac{(1 + F) X_{CO} - x_1}{2n + m} \qquad (16)$$

$$y = X_{CO} - zn \qquad (17)$$

Where P = Total pressure

F = inlet H_2/CO ratio, mole/mole;

Note now z and y are based on per mole of CO entering the reactor.

Summary of Procedure of Kinetic Model Selection

(a) Conduct experiments by using the same catalyst and at the same temperature, but varying the feed rate and/or H_2/CO inlet ratio, to get a series data points;

(b) From the analysis of hydrocarbon products find the mean carbon number, n, the H/C ratio and thus m. A mass weighted average value can be taken of the various product streams (Ledakowicz et al, 1985);

278

(c) Find z and y and then the partial pressures using Equations (12) through (17);

(d) Calculate the concentrations by Henry's law, Equation (10);

(e) Test the validity of a specific model by plotting the data of concentrations in proper coordinates. If valid, get the rate parameters b's.

Effect of Temperature

So far the effect of temperature has not been discussed except for that on the Henry's constant. The temperature effect on the rate parameters b's in the kinetic models are usually expressed by the Arrhenius equation,

$$b_i = A_i \exp\left(-\frac{E_i}{T}\right) \qquad (18)$$

Therefore by conducting experiments at several temperature levels and repeating the calculation procedure outlined above, we can get the variation of b's with temperature and find the frequency factor A's and the activation energy E's in Equation (18). By now, a complete kinetic model is established.

CSTR MODEL

All of the kinetic models discussed above can be written in a common form:

$$-r_{CO-H_2} = k C_E \qquad (29)$$

See earlier equation 8
Also more complicated cases. See next page

279

where k can be called reaction rate parameter. Unlike the rate constant in the first order expressions, k is a parameter which varies according to different kinetic models. Table 1 gives the proper expression of k for each kinetic model mentioned above.

Table 1. Rate Parameter k for Different Kinetic Models

Model	1st order	CO_2 only	H_2O only	CO_2 plus H_2O
k	b_2	$\dfrac{b_1}{1+b_2\dfrac{C_{CO_2}}{C_{CO}}}$	$\dfrac{b_1}{1+b_2\dfrac{C_{H_2O}}{C_{CO}}}$	$\dfrac{b_1}{1+b_2\dfrac{C_{CO_2}}{C_{CO}}+b_3\dfrac{C_{H_2O}}{C_{CO}}}$

Using the rate parameter thus defined, a model correlating the conversions with the system parameters and operation conditions for CSTR reactor can be developed. The principal assumptions for the model is that the mass transfer is infinitely fast. That is, no limitation due to mass transfer is assumed. As a rule of thumb, this is satisfied when the stirer speed is larger than 700 rpm (Ledakowicz et al, 1984).

Note the reaction rate $-r_{CO}$ is based on per unit mass of catalyst, therefore

e.g. get an instantaneous $\frac{mole}{s \cdot gms fe}$ conversion x

rate $\left\{ \begin{array}{c} = \\ CO+H_2 \end{array} \right.$

$$-r_{CO-H_2,m_{cat}} = X_{CO-H_2,O} N^0_{CO-H_2} \qquad (20)$$

where m_{cat} = mass of catalyst, g

N^0_{CO} = molar flow rate of syn-gas at inlet, mole/s.

Using Equation (19) we have

$$kC_{H_2}m_{ca} = X_{CO-H_2}N_{CO-H_2}^0$$ (21)

By Henry's law

$$C_{H_2} = \frac{P_{H_2}}{H_{H_2}} = P\frac{w_{H_2}'}{H_{H_2}}$$ (22)

H = Henry's Constant

where w_{H_2}' is the molar fraction of H_2 at the outlet. Material balance of H_2 gives:

$$w_{H_2}'N' = w_{H_2}^0 N_{CO-H_2}^0 (1-X_{H_2})$$ (23)

where $N'=PQ'/RT$, the molar flow rate of gas phase at the outlet, mol/s, with Q' being the volumetric flow rate at the outlet, m'/s. Using the relations

$$Q' = Q_{CO-H_2}^0 (1+\alpha X_{CO-H_2})$$ (24)

and

$$w_{H_2}^0 = F/(1+F)$$

where α is the contraction factor, and F is the H_2/CO inlet ratio, mole/mole, we get from Equations (22) and (23),

$$C_{H_2} = \frac{RTN_{CO-H_2}^0}{Q_{CO-H_2}^0 H_{H_2}} \left(\frac{1-X_{H_2}}{1+\alpha X_{CO-H_2}}\right)\left(\frac{F}{1+F}\right)$$ (25)

[handwritten margin notes:]
Lewis thinks outlet conc not needed. If you do need and use outlet H_2 conc to estimate gas phase H_2 then how about all of the gas phase component knocked out by the traps?

Lewis thinks that the conc out or you are relating mole fraction @ outlet to mole fraction at inlet and conversion. So mole fraction at outlet not ∴ not needed ∴ don't need con

281

Substituting Equation (25) in Equation (21) gives

$$\frac{k m_{cat} RT}{H_{H_2} \rho_{CO-H_2}^0} = \frac{X_{CO-H_2}(1+\varepsilon X_{CO-H_2})}{1-X_{H_2}}\left(1+\frac{1}{F}\right) \qquad (26)$$

Define the Damkohler number

$$Da = \frac{k m_{cat} RT}{H_{H_2} \rho_{CO-H_2}^0} \qquad (27)$$

and

$$\alpha^* = \alpha \frac{F(1+U)}{U(1+F)} \qquad (28)$$

where U is the H_2/CO usage ratio. Also notice the relation between the conversions:

$$X_{CO-H_2} = \frac{F(1+U)}{U(1+F)} X_{H_2} \qquad (29)$$

We finally get the desired model for CSTR reactors:

$$\frac{(1+1/U) X_{H_2}(1+\varepsilon^* X_{H_2})}{1-X_{H_2}} = Da \qquad (30)$$

No Mass Transfer limitations

Lewis plotted this equation which ~ linear only wh~ first order. Used data set f~ Run 43

282