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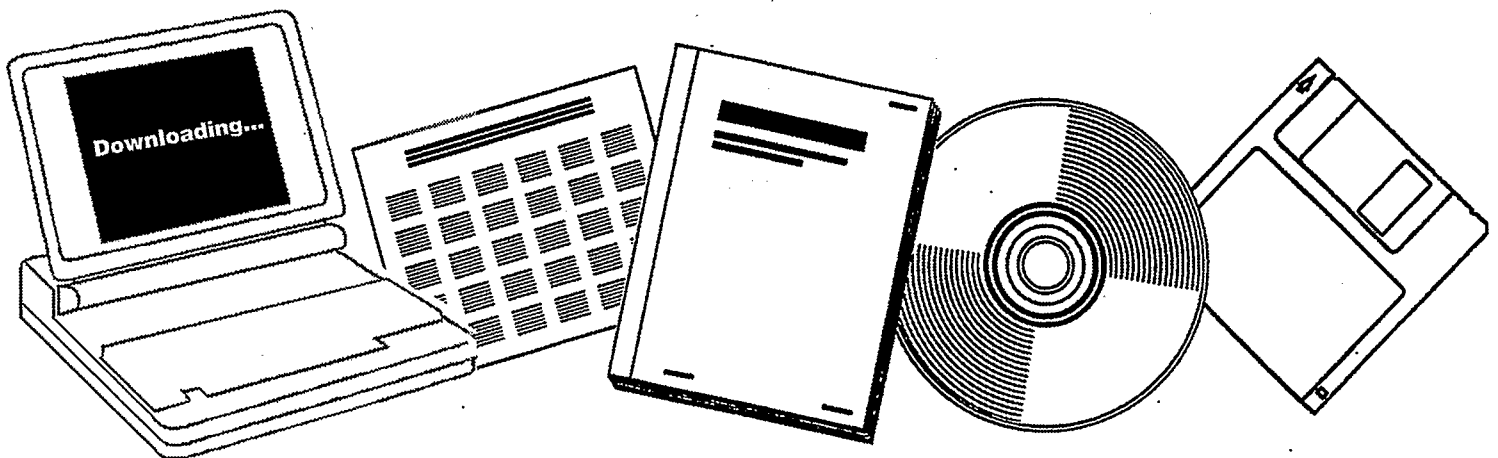
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**SLURRY FISCHER-TROPSCH/MOBILE TWO-STAGE
PROCESS OF CONVERTING SYNGAS TO
HIGH-OCTANE GASOLINE. QUARTERLY REPORT, 1
OCTOBER-31 DECEMBER 1981**

**MOBIL RESEARCH AND DEVELOPMENT CORP.
PAULSBORO, NJ**

JAN 1982



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SLURRY FISCHER-TROPSCH/MOBIL TWO-STAGE PROCESS
OF CONVERTING SYNGAS TO HIGH OCTANE GASOLINE

QUARTERLY REPORT FOR THE PERIOD
1 OCTOBER - 31 DECEMBER, 1981

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I. Abstract

The construction of the BSU has been completed and the shakedown of the BSU has been initiated.

A preliminary operating manual for the BSU has been prepared. A material balance program has also been written to handle the operating and product data obtained during the BSU operation.

An improved F-T bubble-column mathematical model has been developed to include multi-component (H_2 , CO, CO_2 , and H_2O) diffusion, a complex kinetic expression for the F-T reaction, and a water-gas shift reaction. An orthogonal collocation method has been used to solve the resulting non-linear equations numerically. Kinetic constants of a precipitated Fe-catalyst have been estimated using the model based on a set of published conversion data. Parametric studies of varying superficial gas velocity, Fe-catalyst loading in the reactor slurry, and feed H_2/CO ratio have been performed to predict their effect on the F-T bubble-column performance.

II. Objective and Scope of the Project

The overall objective of the contract is to develop a two-stage slurry Fischer-Tropsch/ZSM-5 process for direct conversion of syngas, of the type produced in a coal gasification system, to high octane gasoline. The specific objective is to design, construct, and operate a bench-scale pilot plant so that the economic potential of this process concept can be evaluated. To accomplish these objectives, the following specific tasks will be undertaken:

Task 1 - Design of Bench-Scale Pilot Plant

A two-stage slurry F-T/ZSM-5 bench-scale pilot plant will be designed for conversion of syngas to high octane gasoline. The slurry F-T reactor will be 2" ID and 25' high. The fixed-bed ZSM-5 reactor will be 2" ID and 4-18" high. A distillation column will be designed to obtain stabilized gasoline products.

Task 2 - Construction and Shakedown of Pilot Plant

The pilot plant will be constructed in MRDC Paulsboro Laboratory. The unit will be shaken down when completed.

Task 3 - Operation of Pilot Plant

At least three slurry F-T catalysts will be tested in the bench-scale pilot plant. One of these catalysts may be provided by DOE's alternate catalyst development projects. The best first-stage catalyst together with a ZSM-5 class zeolite catalyst will be used for process variable studies and catalyst aging tests in the bench-scale unit. Products obtained from the unit will be evaluated to define their qualities.

Task 4 - Conceptual Design Study

A preliminary conceptual design of the process will be developed for a commercial size plant for the conversion of syngas to high octane gasoline. Scoping costs of the plant will be estimated.

III. Summary of Progress to Date

The construction of the BSU has been completed one week ahead of schedule. The shakedown of the BSU has also been initiated.

A preliminary operating manual for the BSU has been prepared. A material balance program has also been written to handle the operational and product data obtained during the BSU operation.

An improved F-T bubble-column mathematical model has been developed to include multi-component (H_2 , CO, CO_2 , and H_2O) diffusion, a complex kinetic expression for the H_2 and CO conversion, and a water-gas shift reaction. The kinetic constants of a precipitated Fe-catalyst have been estimated using the model based on a set of published data from a small bubble-column. Compared with the result from the previous simple mathematical model, the current model predicted a higher conversion activity in the low to medium H_2+CO conversion region and a substantially lower conversion activity in the high H_2+CO conversion region. Parametric studies of varying superficial gas velocity, Fe-catalyst loading in the reactor slurry, and feed H_2/CO ratio have also been performed to evaluate their effect on the bubble-column performance. Both the superficial gas velocity and the Fe-catalyst loading have a large effect on the column performance; while the feed H_2/CO ratio has only a small effect except in the high H_2+CO conversion region. However, the feed H_2/CO ratio has a significant effect on the reactor exit H_2/CO ratio, which may, in turn, affect the catalyst stability and the methane formation rate.

IV. Detailed Description of Technical Progress

A. Task 2 - Construction and Shakedown of Pilot Plant

1. Status of Task

The construction of the BSU has been completed, a preliminary pressure-test at room temperature has been successfully carried out, and the shakedown of the unit has been initiated one week ahead of schedule.

The process piping for the unit has been under progress in the last quarter. The instrumentation and electrical wiring of the unit have also been initiated. Figure 1 of the last quarterly report (#4) showed the bare unit without any insulation. All heat-tracing and steam-tracing have also been carried out. All vessels, including the reactors and all the heated lines, have been insulated. A photograph of the completed unit is shown in Figure 1. Figure 2 shows the two completed fixed-bed reactors. The top-view of the three sections can also be seen. A ground-level view of the same three sections is shown in Figure 3. Some major vessels, piping, and valving are clearly shown in the figure.

The electrical work as well as the instrumentation for the unit has been completed. All instruments have been mounted on the control panel seen in the left-bottom corner of Figure 1. On the left section of the control panel, nine Liquid-Indicator-Controllers (LICs), five Flow-Indicator-Controllers (FICs), and three Pressure-Indicator-Controllers (PICs) are located. The twenty-three Temperature-Indicator-Controllers (TICs) with eight Adiabatic- Temperature-Controllers (ATCs) are mounted on the middle and right sections of the panel. The two digital temperature indicators can display temperatures at eighty-four different locations around the unit. The important temperatures, such as those of the reactors and condensers, are recorded by the computer for permanent storage.

Any alarm condition at the unit, such as high temperature, high pressure, or gas leaks, sets off an alarm-siren at the control panel and necessary actions will be taken automatically. For example, in the case of excessive temperature rise in the slurry reactor, the heater for the circulating-oil would be turned off and the cooling water turned on. Similarly, when a H₂ or CO gas leak is detected, the alarm circuit would shut off the gas feed as well as the power to the unit.

To recapitulate the construction phase of the project, the off-site construction of vessels was initiated in March 1981 immediately after the detailed engineering drawings were

completed. The on-site construction began in July 1981 with the erection of the steel-structure for the slurry reactor. A total of 106 vessels, 607 valves, 19 pneumatic control valves, 25 pressure gauges, and 123 thermocouples are used in BSU. Also, ninety-seven engineering drawings were prepared for this job. The construction was completed one week ahead of schedule. A preliminary pressure-test was also carried out as part of the construction. The shakedown of the unit was, therefore, initiated one week ahead of schedule and will continue into the next quarter.

2. Conclusion

The construction of the BSU has been completed one week ahead of schedule and subsequently the shakedown of the BSU has also been initiated.

3. Future Work

- e To complete the unit shakedown in the next quarter.
- e To carry out any necessary maintenance and modification.
- e To start-up the unit.

B. Task 3 - Operation of Pilot Plant

1. BSU Operating Manual and Material Balance Program

A preliminary operating manual for the BSU has been prepared describing step-by-step procedures for all phases of the unit operations. It will be used by operators as a basic operational guide. The specific operating conditions along with special instructions will be provided by the engineer during each run.

The preliminary manual includes many procedures. The most important of these are: Safety, Pre-Start-Up, Start-up and Shut-down, and Material-Balance Procedures. The Safety Procedures emphasize on the special care required for the safe handling of flammable H_2 , poisonous CO , and the hot wax-slurry. The Pre-Start-Up Procedures describe the procedures such as the slurry reactor cleaning and slurry preparation. The Start-up and Shut-Down Procedures describe the start-up and shut-down of the unit in three different modes. In Mode A, only the first-stage slurry reactor is in operation. In Mode B, one of the fixed-bed reactors is put into operation and in Mode C, the distillation column is in operation in addition to the Mode B operation. The

Material Balance Procedure describes the steps for taking material balances.

A material balance program has been written in APL computer language to handle the operational and product data from the BSU operation. The program has been successfully tested. It is written in such a fashion that an operator can input the necessary data into the program and obtain a complete printed output. All data along with the calculated output is stored in files so that it can be retrieved easily for further analysis.

A 718-component analytical-data-base has also been developed to cover all products of single-stage or two-stage process. This data base is used to report the composition of different product-streams and is also used in the material balance program.

The program is rather complex because it involves interfacing between four product streams and also interfacing between a variety of analytical methods necessitated by different product streams. The only data for input by an operator is the operating-information data such as reactor pressure, temperature, gas-feed rates and rate of different product streams. The program then retrieves the product compositions stored in the analytical data-base. It then completes the balance calculations, and and both prints out and stores the results in the computer. Appendix A gives a sample output of the program for F-T products. Page 1 of the output gives details of feed and products. Page 2 gives the detailed breakdown of product yields and selectivity. Page 3 shows the summary of product yield and selectivity. The program is versatile enough to be used for either single-stage or two-stage operation.

2. Fischer-Tropsch Bubble-Column Mathematical Model and Applications

a. An Improvement of the Existing Mathematical Model

In previous quarterly reports, the F-T bubble-column mathematical model was constructed based on a single reactant component (H_2), and a single first-order F-T kinetic expression (for example, see Equation (1) of the October-December 1980 Quarterly Report). This simple approach allows a quick way of solving the associated mathematical equations. However, these simple-minded assumptions gave inexact descriptions of the transport phenomena and the kinetics of the system. For example, since the H_2 diffusivity is substantially higher than the diffusivities of CO and other components, the mass transfer resistance in a single-component model was less than that which occurs in a multi-component system. Furthermore, a first-order kinetics gave an overly optimistic prediction on the H_2+CO

conversion at high conversion regions where the kinetics approached second-order according to Dry (1976). The current mathematical model includes multicomponent (H_2 , CO , CO_2 , and H_2O) diffusion and a complex kinetics for H_2 and CO conversion due to F-T reactions. It also includes a separate water-gas shift reaction which describes a kinetic conversion of CO to H_2 using the H_2O formed in the F-T reactions.

Major assumptions of the current mathematical model are:

1. Plug-flow gas-and non-mixing liquid-phase.
2. Uniform catalyst distribution in liquid-phase.
3. Mass-transfer resistance only at liquid side of gas-liquid interface.
4. Constant molar contraction due to F-T reactions.
5. A single F-T reaction of the following stoichiometry and kinetic expression (Dry, 1976) are used to describe the complex F-T reactions:



$$r_1 = k_1[H_2] [CO] / ([CO] + k_3 [H_2O]) \quad (2)$$

6. Following water-gas shift reaction and kinetic expression (Newsome, 1980):



$$r_2 = k_2([CO] [H_2O] - [H_2][CO_2]/k_A) / ([CO] + k_3[H_2O]) \quad (4)$$

where k_A is the equilibrium constant for the water-gas shift reaction.

7. Constant bubble-size but with variable gas-holdup and gas-liquid interfacial surface area along the reactor length.
8. Steady-state and isothermal operation.

In the rate expressions (2) and (4), [] signifies volumetric concentrations. Note that the same denominator expression is used in both rate expressions. This is consistent with the hypothesis of competitive adsorption of active species on the same catalytic active sites (Langmuir-type adsorption isotherm)

[Satterfield, 1980]. Only the [CO] and [H₂O] appearing in the denominator indicate that both are strongly adsorbed on the catalyst active sites.

Material balances for the gas- and liquid-phase of the components H₂, CO, CO₂ and H₂O (denoted by subscripts 1, 2, 3, 4, respectively), yield:

$$d(u_g C_{gi})/dz + k_{li} a_g (C_{gi}/K_i - C_{li}) = 0, \quad i = 1, \dots, 4 \quad (5)$$

for the gas-phase, and

$$k_{li} a_g (C_{gi}/K_i - C_{li}) + (1 - \epsilon_g)(1 - v) C_{Fe} \sum S_{ij} r_j = 0, \quad i = 1, \dots, 4 \quad (6)$$

for the liquid-phase, with the following inlet conditions:

$$C_{gi} = C_{gi}^i \text{ at } z = 0, \quad i = 1, \dots, 4 \quad (7)$$

where r_1 and r_2 are, respectively, the F-T and the water-gas shift reaction rates given by Equations (2) and (4), and S_{ij} ($i = 1, \dots, 4$; and $j = 1, 2$) are elements of the stoichiometric matrix.

Assuming that the molar contraction due to the F-T reaction is linear with respect to the H₂+CO conversion, the following relation between the gas superficial velocity and the H₂+CO conversion was obtained:

$$u_g = u_g^i (1 + \alpha X_{H_2+CO}) \quad (8)$$

where α is the constant molar contraction factor. In deriving Equation (8), it is assumed that the pressure and the temperature are uniform along the reactor length.

In dimensionless form, Equations (5) to (7) become:

$$d(u_g C_{gi})/dz + St_{di}(C_{gi} - C_{li}) = 0 \quad (9)$$

$$St_{di}(C_{gi} - C_{li}) + \sum S_{ij} St_{kj} r_j = 0 \quad (10)$$

$$C_{gi} = C_{gi}^i \text{ at } z = 1 \quad (11)$$

for $i = 1, \dots, 4$.

A solution for this set of non-linear equations can be obtained using the orthogonal collocation method (Villadsen and Michelsen, 1978). This method dictates that the trial solutions (linear combinations of orthogonal polynomials described in the Quarterly Report #4 (July-Sept., 1981)) satisfy the gas-phase and the liquid-phase equations exactly at the N interior collocation points, the inlet point, and the exit point. This results in a system of $8N+12$ non-linear algebraic equations, which are solved

simultaneously by a Newton-Raphson routine. The convergence criterion of the iterative scheme is that the successive dependent variables at all collocation points be within 0.1% of each other. It was found that five collocation points were sufficient in most calculations as shown in Figure 4.

Note that using variable gas holdup and interfacial area along the reactor length gives virtually identical results as the case of an average gas holdup and interfacial area. (See Figure 7 of the Quarterly Report #2 (January-March, 1981)). In the current case, the use of variable gas holdup and interfacial area actually simplifies the numerical iteration scheme, avoiding the necessity of an additional iteration on the parameters St_{kj} and St_{di} (which are dependent on ϵ_g and a_g).

b. Estimate of Kinetic Parameters From A Set of Published F-T Column Data

A set of literature data from a bench-scale F-T bubble-column was used to estimate the kinetic parameters of a precipitated Fe-catalyst (Koelbel and Ralek, 1980). The operation conditions of this data set were summarized in Table 1. In addition to these conditions, the solubilities and diffusivities of all four components were estimated either from experimental data or correlation equations as summarized in Table 2. The correlations used to calculate the liquid-side mass transfer coefficient, gas holdup, and liquid density and viscosity were the same as those used in previous Quarterly Reports (Deckwer, et al., 1980). Values of bubble size, catalyst solid density, iron fraction in the catalyst, and molar contraction factor were also the same as those used in previous Quarterly Reports. Those parameters were summarized in Table 3 as the base case.

The numerical scheme used to estimate the kinetic parameters was the method of parametric regression to minimize the following target function:

$$(1 - (X_{H_2+CO})_{calc}/(X_{H_2+CO})_{exp})^2 + (1 - U_{cal}/U_{exp})^2 \quad (12)$$

The convergence criterion was that this target function was less than 10^{-5} . The resulting kinetic parameters were included in Table 3.

Because of the complex kinetic expression used in the current improved model, it was not straight forward in comparing the current kinetic constants with the single constant obtained in the previous single-component (H_2) kinetic expression. Using Equation (2), the rate expression for the F-T reaction will be reduced to the simple first order kinetic expression used in the preceding Quarterly Reports when $[CO] \gg k_3[H_2O]$. This happened at

the entrance portion of a F-T bubble-column when a dry synthesis gas was used. However, the rate becomes minute when $[\text{CO}]$ and $[\text{H}_2]$ become small. This description indicates that the $\text{H}_2 + \text{CO}$ conversion rate at the entrance part of a bubble-column was higher than that which was predicted using the earlier first-order kinetic model. Nevertheless, when the synthesis gas conversion proceeds, the conversion rate approaches second-order kinetics, and the rate becomes significantly lower. This observation is clearly illustrated in Figure 5. The constants k_2 and k_4 describe the rate of the water-gas shift reaction (Equation (4)) and significantly affect the H_2 , CO , H_2O , and CO_2 concentration along the reaction path. The estimated equilibrium constant k_4 (34.7) matches exactly the equilibrium constant given by Newsome (1980).

Figures 6, 7, and 8 illustrate some interesting information obtained from this case of kinetic constants estimation (conditions listed in Table 1). Figure 6 shows the variation of H_2 , CO , CO_2 , and H_2O concentrations in both the gas- and the liquid-phase along the bubble-column. Note that CO_2 concentrations increase quickly along the column because the water-gas shift reaction favors the CO_2 formation under the given conditions. Also, the H_2O concentration varies only a little after the entrance portion of the column since the rate of its dissipation by the water-gas shift reaction is approximately balanced by its rate of formation due to the F-T reaction. Figure 7 shows the variation of the F-T and water-gas shift reaction rates along the column. The F-T rate decreases quickly along the reaction path. Figure 8 shows the H_2/CO ratios in both the gas- and liquid-phase along the column height. Along most of the column, the H_2/CO ratio in the liquid-phase is higher than that of the gas-phase because the H_2 mass transfer coefficient is substantially larger than that of the CO . It is interesting to see that the H_2/CO ratio has a minimum, and that the water-gas shift reaction rate and the H_2O concentrations have a maximum along the column height. All these phenomena can be properly explained by the existence of the water-gas shift reaction.

The question of how important is the mass transfer resistance across the gas-liquid interphase becomes more complex for the multi-component system. Nevertheless, a single component (H_2) model may under-predict a gas-liquid mass transfer resistance, since H_2 has the highest diffusivity (about 6.5 times that of the CO) among the four components used in the current model.

c. Parametric Studies Using the Mathematical Model

Parametric studies were performed using the current mathematical model and the parameters listed in Table 3. The parameters studied were the superficial gas velocity, the

Fe-catalyst loading in the reactor slurry, and the feed H_2/CO ratio. Figure 9 shows that the superficial gas velocities have a large effect on the F-T bubble-column performance. The predicted reactor length becomes substantially longer with higher gas velocity. Figure 10 shows that the Fe-catalyst loadings also exerts a significant effect on the F-T bubble-column performance. An increase of Fe-loading from 5 wt% to 10 wt% strongly affects the F-T column performance; however, the effect resulting from an increase of the loading from 10 wt% to 15 wt% is considerably less. Figure 11 shows that the effect of varying feed H_2/CO ratios on the F-T bubble-column performance is not significant except in the high H_2/CO conversion region. The varying feed H_2/CO ratio affects the reactor exit H_2/CO ratio in the high H_2+CO conversion region as indicated in Figure 12. This may somewhat affect the catalyst aging and the methane formation rate, both of which varies with the H_2/CO ratio in the gas-phase.

3. Conclusions

A preliminary operating manual for the BSU has been prepared. A material balance program has also been written to handle the operational and product data obtained in the future BSU operation.

An improved F-T bubble-column mathematical model has been developed to include multi-component (H_2 , CO , CO_2 , and H_2O) diffusion, a complex kinetic expression for the F-T reaction, and a water-gas shift reaction. The resulting non-linear equations were solved numerically using an orthogonal collocation method. Kinetic constants of a precipitated Fe-catalyst have been estimated using the model based on a set of small bubble-column data from Koelbel (Koelbel and Ralek, 1980). When compared with the previous single-component, first-order kinetic mathematical model, the current model predicts higher conversion activity in the low to medium conversion region; but substantially lower conversion activity in the high conversion region. Using these kinetic constants, parametric studies of varying superficial gas velocity, Fe-catalyst loading in the reactor slurry, and feed H_2/CO ratio have been performed with the following conclusions on their effect on F-T bubble-column performance:

- Both the varying superficial gas velocities (2, 4, 6 cm/s) and the varying Fe-catalyst loadings in the reactor slurry (5, 10, 15 wt%) have a large effect on the F-T bubble-column performance. However, the effect due to increasing the catalyst loading from 10 wt% to 15 wt% is considerably less than the similar effect due to increasing the catalyst loading from 5 wt% to 10 wt%.

- The effect of varying feed H_2/CO ratios (.6, .7, and .8) on the F-T bubble-column performance is not significant except in the high H_2+CO conversion region. The reactor exit gas H_2/CO ratio also increases significantly with varying feed H_2/CO ratios when the H_2+CO conversion is high. This may somewhat affect the catalyst aging and the methane formation rate, both of which depend on the H_2/CO ratio in the gas-phase.

4. Future Work

- The BSU operating manual will be updated and improved.
- The phase of F-T catalyst evaluation in the BSU will be initiated.
- The F-T bubble-column mathematical model will be updated and improved and will be used to assist the BSU operation.

V. NOMENCLATURE

a_g	Gas bubble interfacial area, $6\epsilon_g/d_B$, (cm^2 gas-liquid area/mL expanded slurry)
C_{Fe}	Iron loading, (gFe/mL liquid)
C	Concentration, (mol/mL liquid or gas)
\bar{C}_g	C_g/C_{g1}^i
\bar{C}_l	$C_l K/C_{g1}^i$
D_l	Liquid-phase diffusivity, (cm^2/s)
d_B	Bubble diameter, (cm)
f	H_2/CO at reactor inlet
f_{Fe}	Weight fraction of Fe in catalyst
K	Solubility coefficient, (mL liquid/mL gas)
k_1, k_2	Intrinsic kinetic rate constants for F-T and water-gas shift reactions, respectively, used in Equations (2) and (4), (mL liquid/s-gFe)
\bar{k}_2	$k_2 K_1/K_4$, (mL liquid/gFe-s)
k_3, k_4	Constants used in the rate expressions (2) and (4)
\bar{k}_3	$k_3 K_2/K_4$
\bar{k}_4	$k_4 K_1 K_3/K_2 K_4$
k_l	Liquid side mass transfer coefficient, (mL liquid/s-(cm^2 gas-liquid area))
L	Bubble column height, (cm)
m	Average H/C atomic ratio of F-T products
N	Number of interior collocation points
n	Average carbon-number of F-T products
P	Pressure, (mPa)
R_d	Transport resistance from gas-liquid interface to bulk liquid phase, $K/k_l a_g$, (s-mL expanded slurry/mL gas)

R_k	Kinetic resistance, $K/kC_{Fe}(1-\epsilon_g)(1-v)$, (s-mL expanded slurry/mL gas)
r_1	Kinetic rate of F-T reaction, given as Equation (2), (mol/s-gFe)
r_2	Kinetic rate of water-gas shift reaction, given as Equation (4), (mol/s-gFe)
\bar{r}_1	$\bar{C}_{11} \bar{C}_{12} / (\bar{C}_{12} + \bar{k}_3 \bar{C}_{14})$
\bar{r}_2	$(\bar{C}_{12} \bar{C}_{14} - \bar{C}_{11} \bar{C}_{13} / \bar{k}_4) (\bar{C}_{12} + \bar{k}_3 \bar{C}_{14})$
S_{ij}	Elements of stoichiometric matrix, $i = 1, \dots, 4$; and $j = 1, 2$
T	Temperature, ($^{\circ}\text{C}$)
U	H_2/CO usage ratio
u	Superficial velocity, (cm/s)
\bar{u}_g	u_g / u_g^i
v	Volumetric fraction of catalysts in slurry, $\rho_l w / (\rho_s + w(\rho_l - \rho_s))$, (mL catalyst/mL slurry)
w	Weight fraction of catalysts in slurry, (gCat/g slurry)
$X_{\text{H}_2+\text{CO}}$	$\text{H}_2 + \text{CO}$ conversion
z	Reactor vertical distance from its entrance, (cm), z/L
\bar{z}	z/L
	<u>Greek Letters</u>
α	Contraction factor, mole of products per mole of H_2+CO converted
ϵ_g	Gas hold-up, (mL gas/mL expanded slurry)
ρ	Density, (g/mL)
ρ_s	Catalyst solid density, (g/mL)
μ	Viscosity, (g/s-cm)
	<u>Dimensionless Numbers</u>
St_d	Stanton number (diffusion resistance), $L/u_g^i R_d$
St_k	Stanton number (kinetic resistance), $L/u_g^i R_k$

Superscripts

e At reactor exit
i At reactor inlet

Subscripts

c Catalyst
g Gas
i Components, $i = 1, 2, 3, 4$ for H_2 , CO, CO_2 , H_2O ,
respectively
l Liquid
Fe Iron

VI. Literature

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APPENDIX A

SAMPLE OUTPUT OF THE MATERIAL-BALANCE
PROGRAM FOR FISCHER-TROPSCH PRODUCTS

Figure 4

EFFECT OF NUMBER OF COLLOCATION POINTS ON THE
PREDICTED F-T BUBBLE-COLUMN PERFORMANCE
(Base Case)

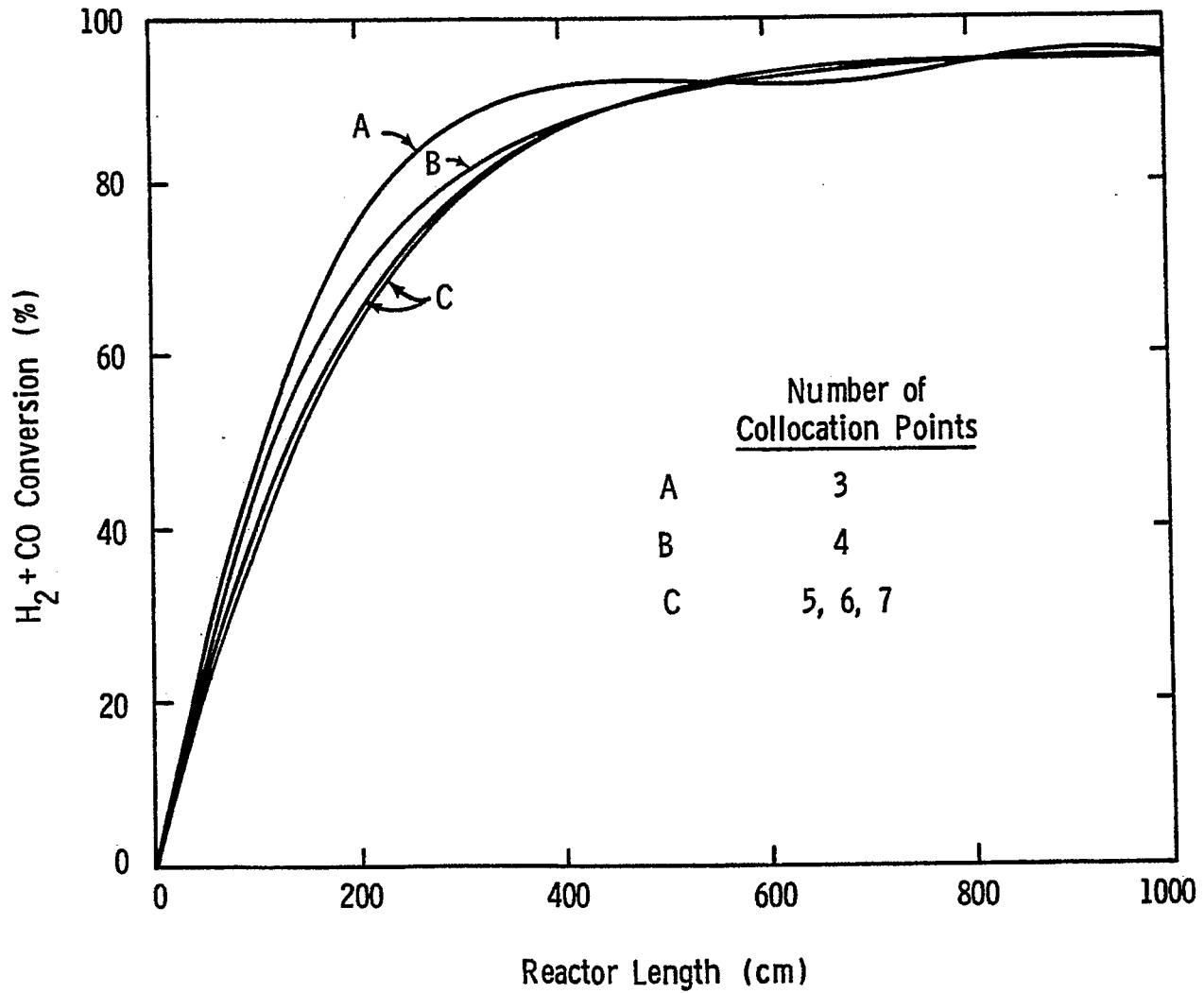
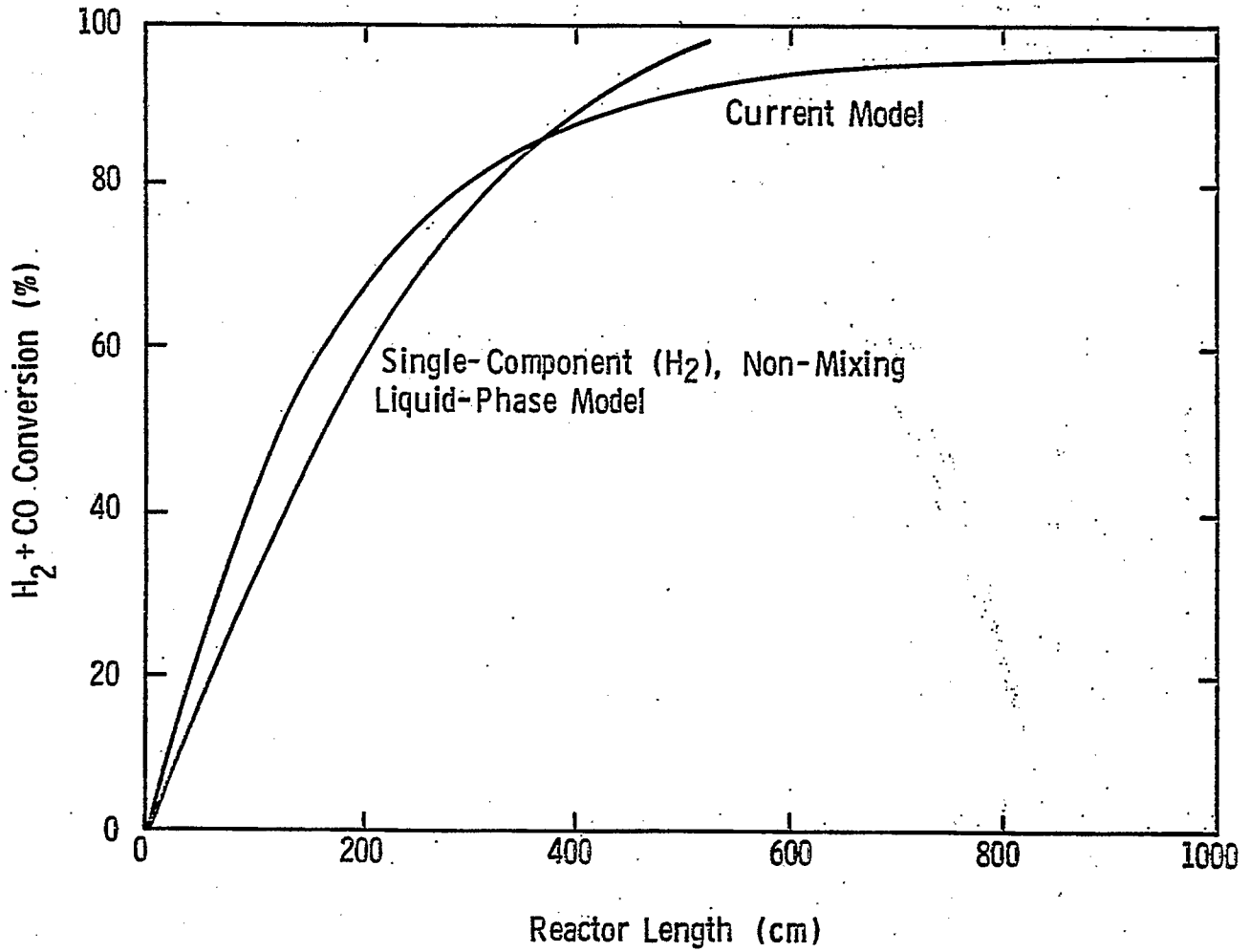


Figure 5

COMPARISON OF CURRENT F-T BUBBLE-COLUMN
MATHEMATICAL MODEL WITH A PREVIOUS MODEL

PREDICTED AXIAL CONCENTRATION PROFILES IN
F-T BUBBLE-COLUMN
(Conditions of Table 1)

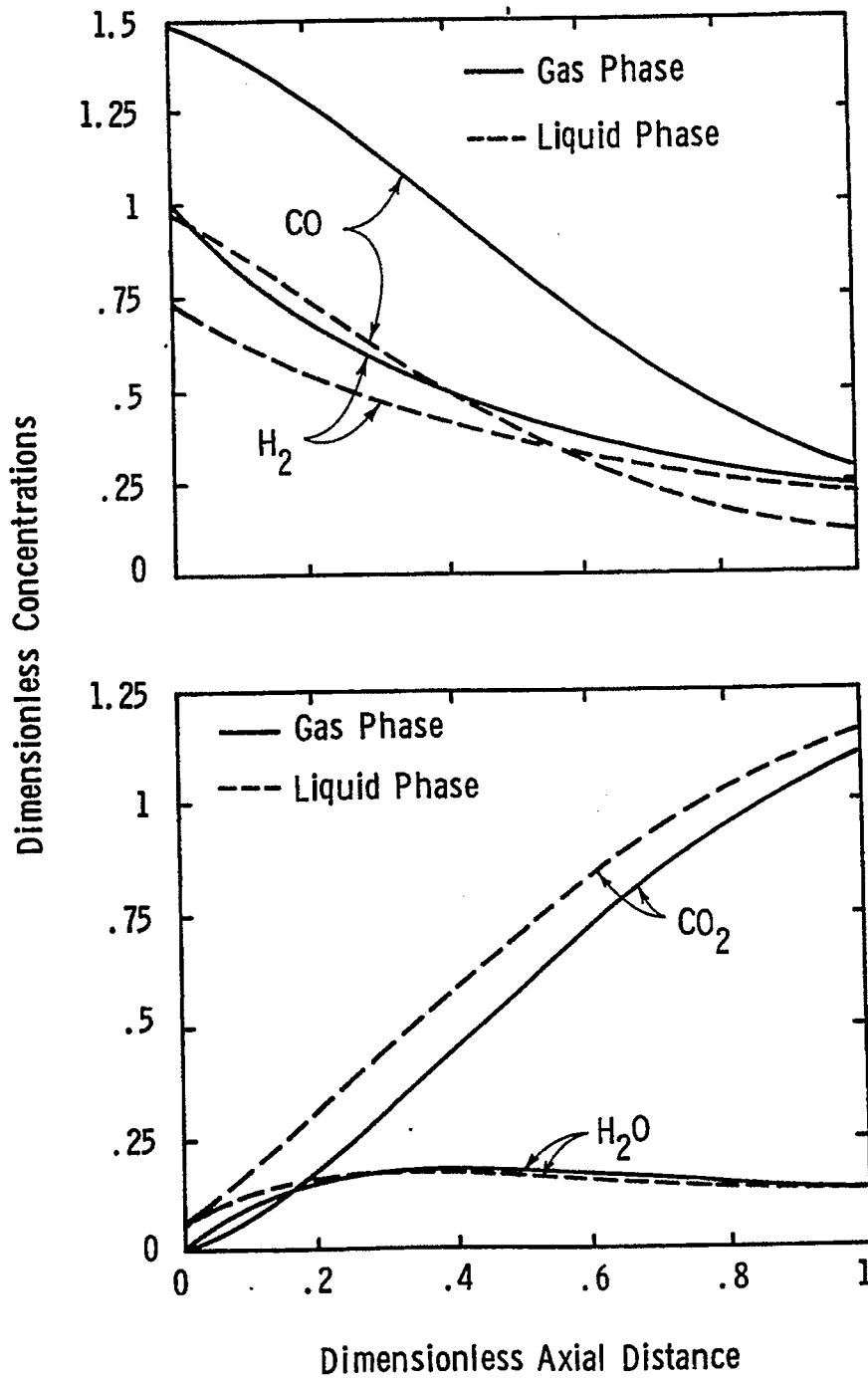


Figure 7

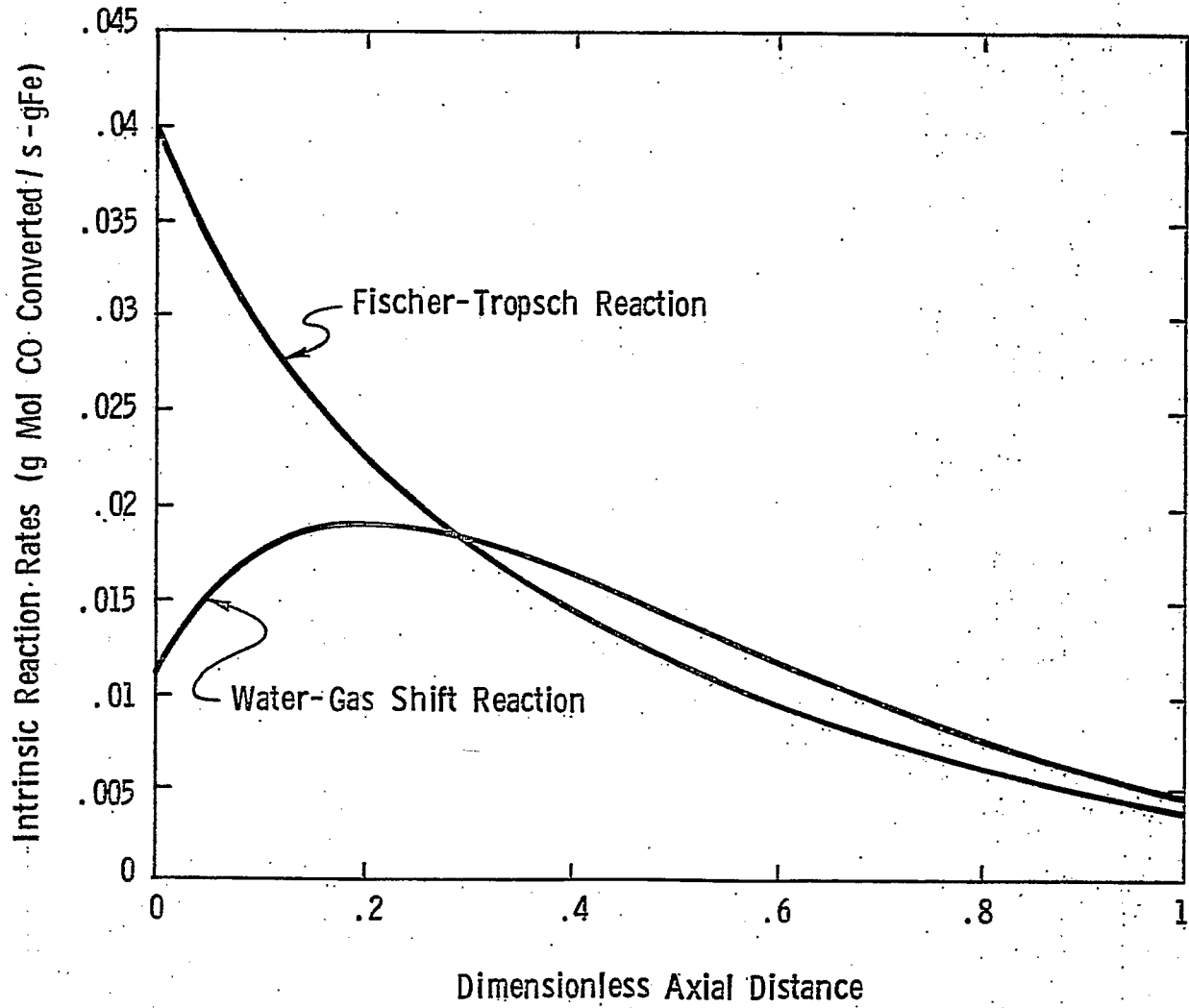
PREDICTED REACTION RATES
(Conditions of Table 1)

Figure 8

PREDICTED H₂ / CO RATIO
(Conditions of Table 1)

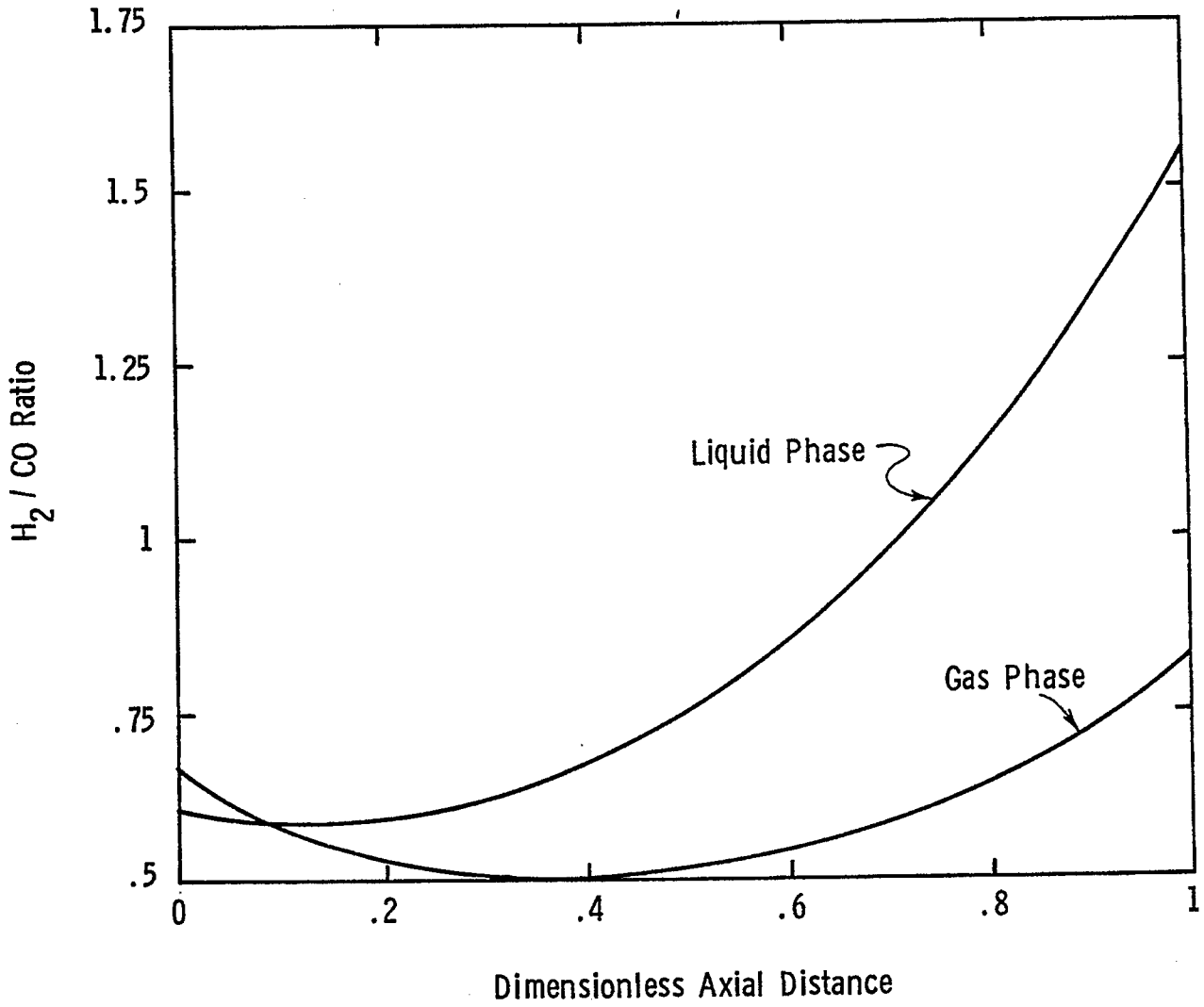


Figure 9

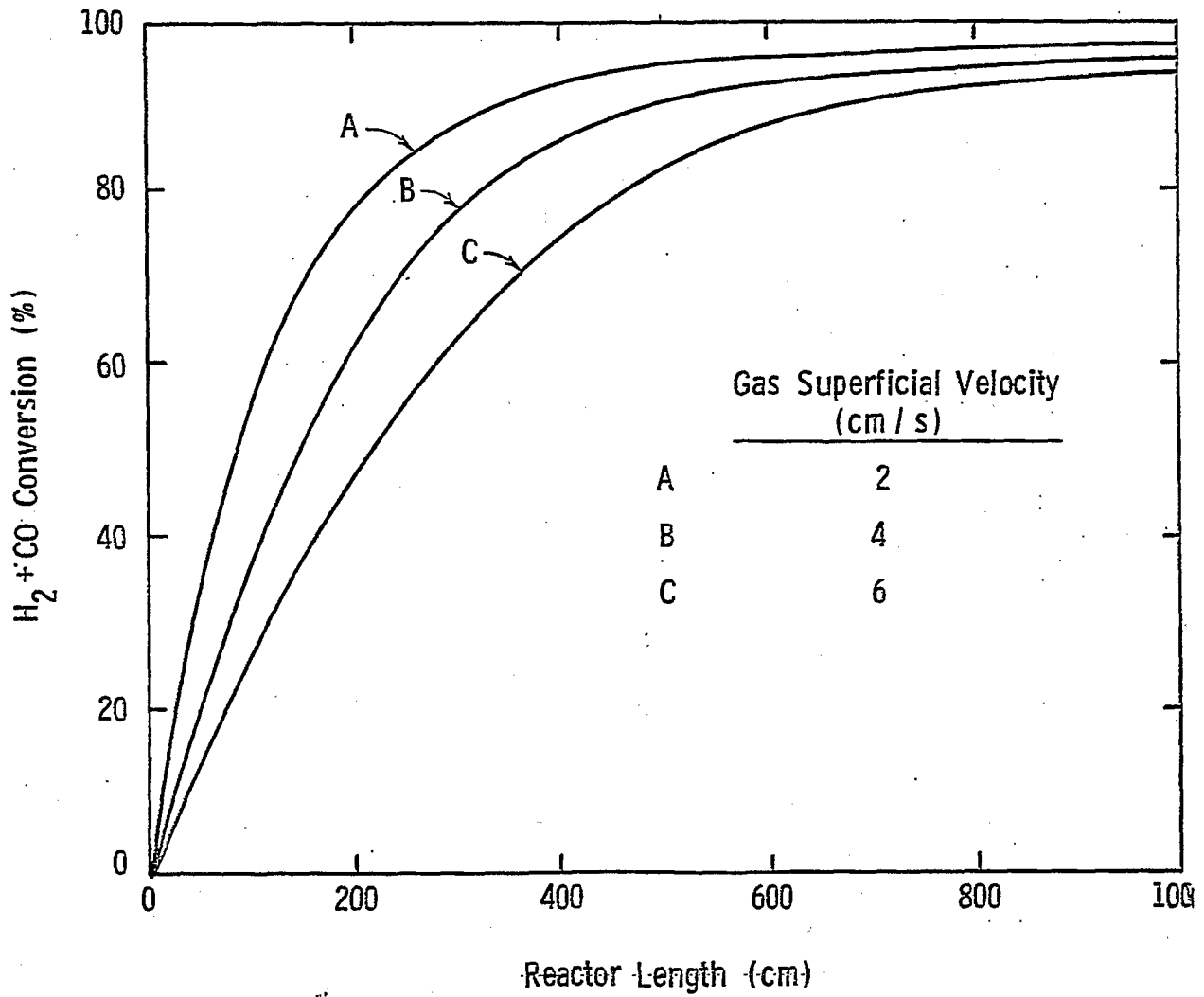
PREDICTED EFFECT OF GAS SUPERFICIAL VELOCITY ON
 $H_2 + CO$ CONVERSION

Figure 10

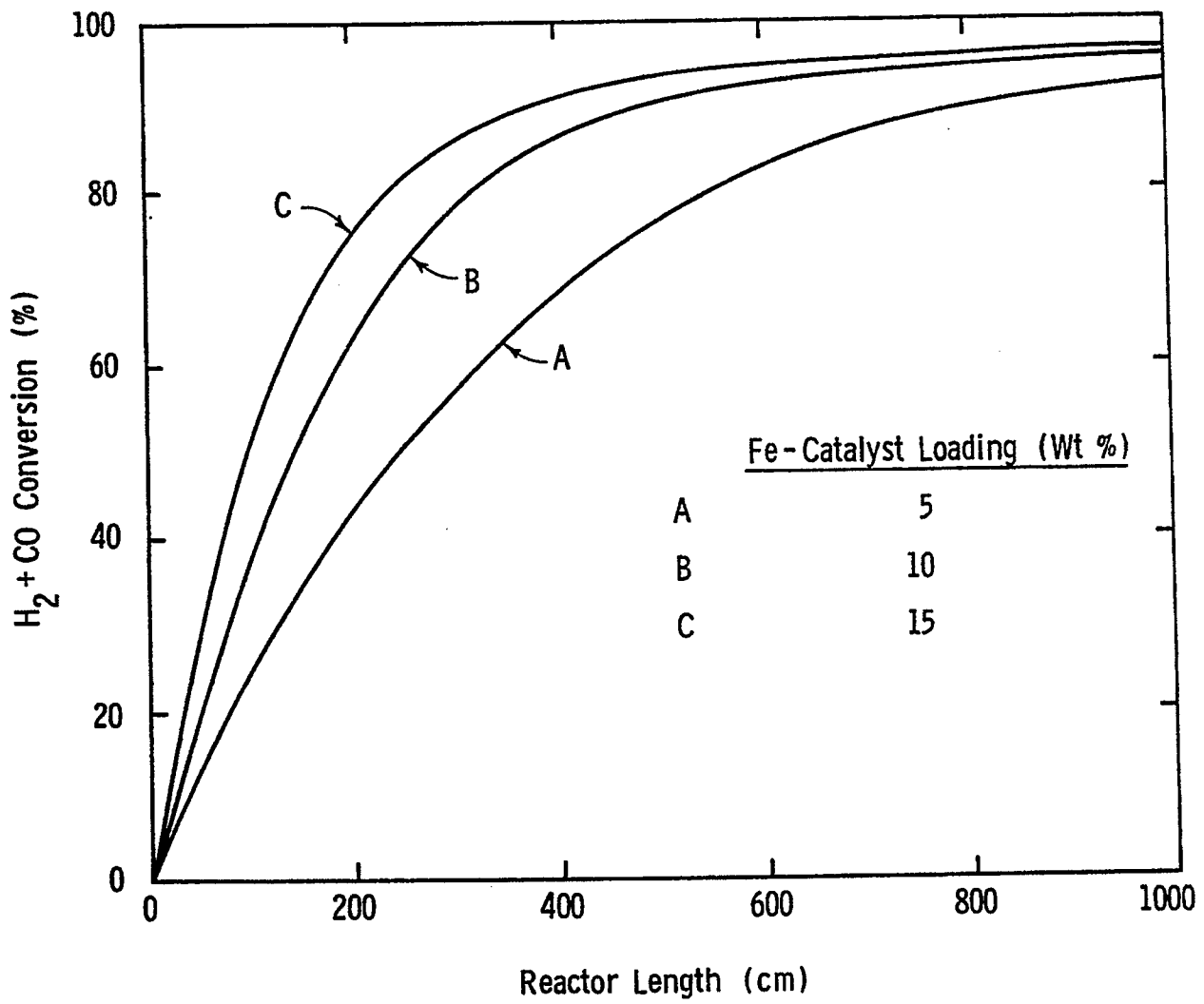
PREDICTED EFFECT OF Fe-CATALYST LOADING ON
 $H_2 + CO$ CONVERSION

TABLE 1

BENCH-SCALE BUBBLE-COLUMN DATA FOR ESTIMATING
KINETICS OF A PRECIPITATED FE-CATALYST (1)

$$T = 266^{\circ}\text{C}$$

$$f = 0.67$$

$$P = 1.1 \text{ mPa}$$

$$f_{\text{Fe}} = 0.67$$

$$u_g^i = 3.5 \text{ cm/s}$$

$$U^e = 0.65$$

$$L = 350 \text{ cm}$$

$$X_{\text{H}_2+\text{CO}} = 88\%$$

$$w_{\text{Fe}} = 10\%$$

$$m = 2.24^{(2)}$$

(1) Koelbel and Ralek (1980).

(2) Probststein and Hicks (1982).

TABLE 2

SOLUBILITY AND DIFFUSIVITY DATA (1)

<u>Solubility (ml liquid/ml gas)</u>	Experimental	Koelbel et al. (1955) Peter & Weinert (1955)
H ₂ 746 T ⁻¹ exp (639.9/T)	"	"
CO 878 T ⁻¹ exp (440.2/T)	"	"
CO ₂ 2970 T ⁻¹ exp (-608.4/T)	"	"
H ₂ O 6740 T ⁻¹ exp (-1270/T)	"	"
<u>Diffusivity (cm²/s)</u>		
H ₂ 3.90 x 10 ⁻² exp (-2877/T)	Experimental + Correlation (2)	Peter & Weinert (1956)
CO 5.99 x 10 ⁻⁴ exp (-1633/T)	Experimental + Correlation (3)	Zaidi et al. (1979)
CO ₂ 3.70 x 10 ⁻⁴ exp (-1437/T)	Experimental + Correlation (2)	Hayduk & Cheng (1971)
H ₂ O 9.6 x 10 ⁻⁴ exp (-1633/T)	Experimental + Correlation	Hayduk & Cheng (1971)

(1) T in °K.

(2) Extrapolation using correlation of diffusivity with liquid viscosity.

(3) Estimates of D₁₂ from correlation produced mass transfer coefficients which fitted experimental data.

TABLE 3

PARAMETERS AND THEIR RANGES ADOPTED IN
THE CURRENT F-T MATHEMATICAL MODEL CALCULATIONS

<u>Operation Parameters</u>	<u>Base Case</u>	<u>Range</u>
T (°C)	265	
$u_{g,i}$ (cm/s)	4	2-6
w_{Fe}	.10	.05-.15
f	.7	.6-.8
<u>Reaction Parameters</u>		
k_1 (ml liquid/s-gFe)	2.09	
k_2 (ml liquid/s-gFe)	1.52	
k_3	.756	
k_4	34.7	
α	-.5	(1)
m	2.24	
<u>Physical Parameters</u>		
K (ml liquid/ml gas)	4.55-3.70-1.78-1.18	(2)
D_{ℓ} (cm ² /s) x 10 ⁻⁴	1.86-.288-.256-.441	(2)
ρ_{ℓ} (g/ml liquid)	.666	
μ_{ℓ} (g/cm-s)	.0225	
ρ_s (g/ml solid)	5.2	
f_{Fe}	.67	

TABLE 3 (Cont'd)

<u>Hydrodynamic Parameters</u>	<u>Base Case</u>	<u>Range</u>
d_B (cm)	.07	
ϵ_g	1.1 .053 (μg)	
k_L (cm/s) $\times 10^{-2}$	3.15-.909-.840-1.21	(2)

(1) Probststein and Hicks (1982).

(2) For H_2 -CO-CO₂-H₂O, respectively.