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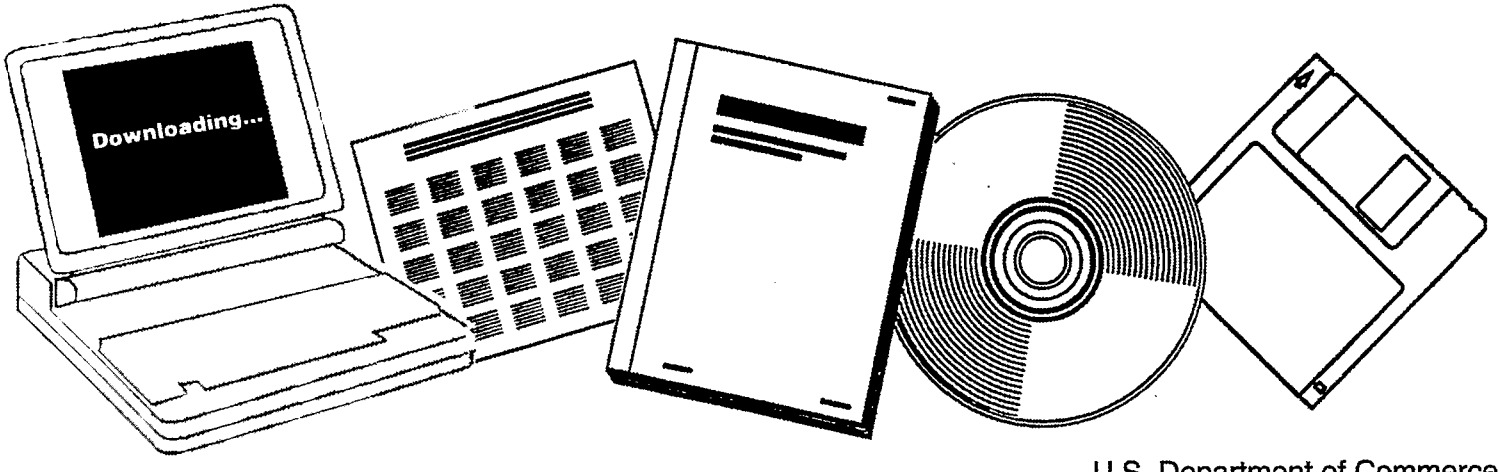
CONVERSION OF LOW H SUB 2 /CO RATIO SYNTHESIS GAS TO HYDROCARBONS. PROGRESS REPORT, OCTOBER 1-DECEMBER 31, 1983

CALIFORNIA UNIV., BERKELEY. DEPT. OF CHEMICAL ENGINEERING

1984



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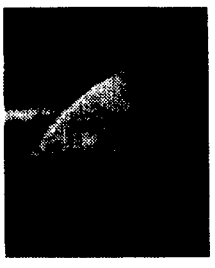

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Conversion of Low H_2/CO Ratio Synthesis Gas to Hydrocarbons

DOE/PC/40795--T1

DE85 008834

Grant No. DE-FG22-81PC40795

Progress Report
for the Period

October 1, 1983 to December 31, 1983

Submitted by

MASTER

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Heinz Heinemann

Department of Chemical Engineering
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ABSTRACT

The rate of CO consumption in a slurry reactor containing a 5% ruthenium on alumina catalyst has been measured at temperatures between 200 and 280°C, pressures from 5 to 12 atmospheres, H_2/CO ratios from 0.4 to 5.0, and superficial gas velocities from 1.8 to 5.2 cm/sec. With this catalyst a Schulz-Flory distribution is not observed.

Variations in the rate with temperature and velocity indicate that mass transfer has only a small influence of the rate of reaction at 280°C. From these results, we estimate that k_La is approximately 0.19 s^{-1} at a superficial gas velocity of 1.9 cm/sec.

Experiments aimed at determining the extent to which mass transfer influences the performance of Fischer-Tropsch slurry reactors have been carried out using a 5 wt% Ru/Al_2O_3 catalyst. CO conversion was measured as a function of H_2 and CO partial pressures, temperature and gas volumetric flow rate.

Figure 1a shows the rate of product formation as a function of carbon number at 200°C, when P_{H_2} is 5 atm. and P_{CO} is 7 atm. Figure 1b shows the same plot when P_{H_2} is 1 atm and P_{CO} is 5 atm. The expected straight line with y-intercept at $R_{C_n}/R_{C_1} = 1.0$ is not observed in either case. While straight-line behavior is observed for high molecular weight products, the intercept is less than unity and the rates of formation of products containing between 2 and 4 carbon atoms sometimes fall below the line. Note that the intercept moves closer to unity as the H_2/CO ratio decreases. In addition, the deviation of lower molecular weight products from the straight line becomes larger as the H_2/CO ratio decreases. Figures 2a and b show the product distribution when P_{CO} is 5 atm, and P_{H_2} is 5 and 2 atm, respectively. These product distributions show the same behavior with H_2/CO ratio as those shown in Figure 1. As the H_2/CO ratio decreases, the y-intercept moves closer to unity, and the lower molecular weight products deviate more from the straight line extrapolated from heavier products. Power law kinetic parameters were determined from these data. The rate of CO consumption is described by the relationship:

$$R_{CO} = k P_{H_2}^{1.03} P_{CO}^{-.20} \qquad (1)$$

Figure 3 shows the rate of CO consumption as a function of $1/T$. The power law kinetics determined earlier were used to correct the rates for changes in partial pressures with conversion. The low temperature data are well described by an activation energy of 19.1 kcal/mole. However, at 280°C,

the rate of CO consumption is about 20 percent lower than predicted by extrapolating the low temperature rates.

Figure 4 shows the rate of CO consumption as a function of gas superficial velocity at 280°C. The rates have again been corrected for changes in gas composition with conversion. As the velocity increases from 1.8 cm/sec to 5.2 cm/sec, a 20% increase in the rate of CO consumption is observed.

The reason for the observed deviations from Schulz-Flory product distributions is not clear. Re-adsorption and subsequent incorporation of lower molecular weight olefins into growing chains may account for the apparent supression of lighter products. Another possibility is that the kinetic parameters that determine the rate of chain growth relative to chain termination depend on the size of the hydrocarbon chain. Further work in this area is required. Addition of low molecular weight olefins to the feed gas may allow us to determine whether olefins adsorb and participate in chain growth.

The increase in CO consumption rate with gas velocity and the deviation of the rate of CO consumption from its expected value at 280°C can both be attributed to mass transfer resistances in the reactor. The expected influence on the rate of CO consumption can be seen by writing the liquid phase mass balance. R_{H_2} is related to R_{CO} by the ratio of the stoichiometric coefficients:

$$R_{H_2} = \frac{\nu_{H_2}}{\nu_{CO}} R_{CO}.$$

The mass balance is written for H_2 because, as seen in eqn. (1), the rate is not strongly influenced by the CO concentration. In the mass balance shown below, the rate is assumed to be first order in H_2 and independent of CO concentration. This assumption is reasonable, in view of the rate expression in eqn. (1), and allows direct solution for $C_{H_2 L}$.

$$R_{H_2} = k_L a\left(\frac{C_{H_2,G}}{m_{H_2}} - C_{H_2,L}\right) = k_o C_{H_2,L} \qquad (2)$$

Solving for C_{H_2}, and substituting back into equation (2) , we obtain:

$$R_{H_2} = \frac{k_L a\, k_o}{k_o + k_L a}\,\frac{C_{H_2,G}}{m_{H_2}} \qquad (3)$$

When $k_L a \gg k_o$, mass transfer does not influence the rate of reaction, and

$$R_{H_2} = R_{H_2}^{max} = \frac{k_o C_{H_2,G}}{m_{H_2}} \qquad (4)$$

As U_G increases, $k_L a$ increases, but k_o remains constant. Thus, R_{H_2} approaches $R_{H_2}^{max}$ when U_G is large. When the temperature increases, k_o increases, but $k_L a$ remains nearly constant. At high temperature, then, R_{H_2} is expected to be less than $R_{H_2}^{max}$.

We can estimate $k_L a$ using equations (3) and (4), along with the experimental values of R_{H_2} and $R_{H_2}^{max}$. $k_L a$ was estimated to be 0.20 s^{-1} from the variation of R with T and 0.17 s^{-1} from the variation of R with U_G. Both estimates are for a superficial velocity of 1.9 cm/s.

CONCLUSIONS

1) We do not observe a Schulz-Flory product distribution over a Ru/Al_2O_3 catalyst.
2) Mass transfer does not have a strong influence of the rate of the Fischer-Tropsch synthesis in our reactor.
3) $k_L a$ for hydrogen is estimated to be 0.19 s^{-1} when the superficial gas velocity is 1.9 cm/sec.

NOMENCLATURE

$C_{H_2,G}$	Gas phase concentration of H_2, moles/cm^3
$C_{H_2,L}$	Liquid concentration of H_2, moles/cm^3
k	Rate coefficient, atm$^{-0.83}$ (moles/cm^3) sec^{-1}
k_o	First order rate coefficient, sec^{-1}.
k_La	Mass transfer coefficient times interfacial area, sec^{-1}
m_{H_2}	Solubility coefficient for H_2
P_{H_2}	H_2 partial pressure, atm
P_{CO}	CO partial pressure, atm
R_{CO}	Rate of CO consumption, moles CO/sec-cm^3
R_{H_2}	Rate of H_2 consumption, moles H_2/sec-cm^3
U_G	Gas superficial velocity, cm/sec

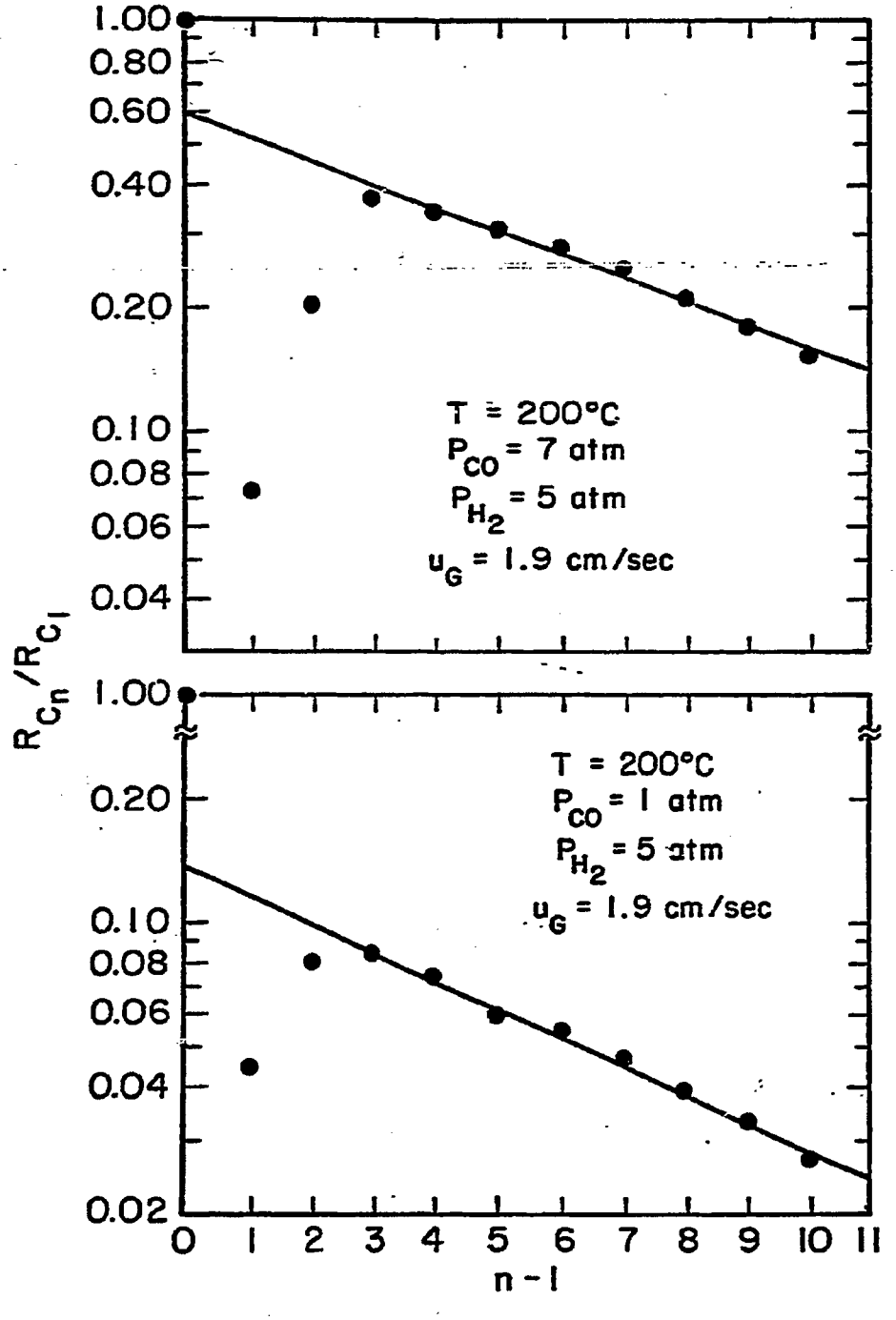
1.00
0.80
0.60
0.40
0.20
0.10
0.08
0.06
0.04
T = 200°C
P_CO = 7 atm
P_H2 = 5 atm
u_G = 1.9 cm/sec
R_Cn/R_C1
1.00
0.20
0.10
0.08
0.06
0.04
0.02
T = 200°C
P_CO = 1 atm
P_H2 = 5 atm
u_G = 1.9 cm/sec
0 1 2 3 4 5 6 7 8 9 10 11
n - 1

Fig. 1

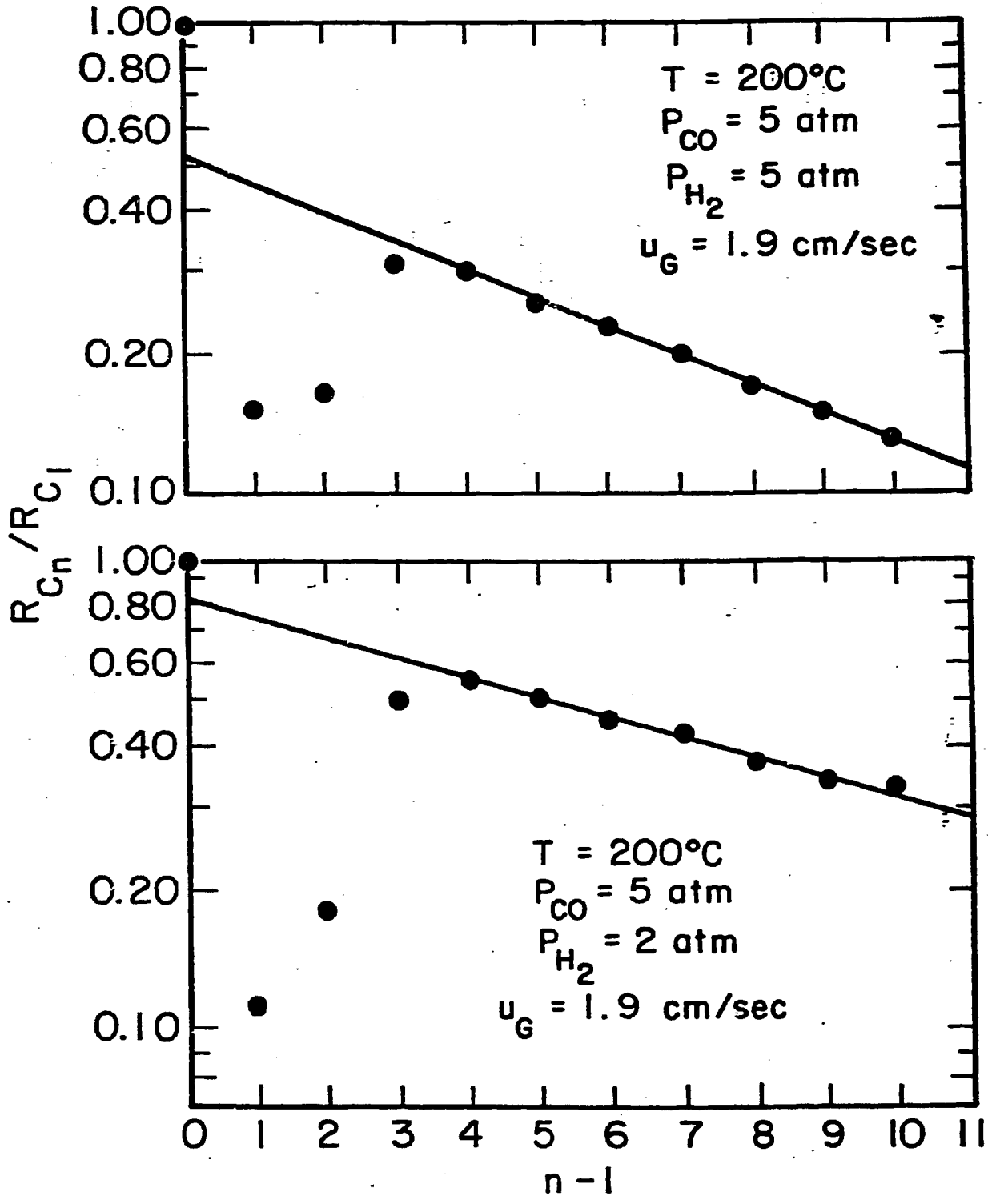
1.00
0.80
0.60
0.40
0.20
0.10
T = 200°C
P_{CO} = 5 atm
P_{H_2} = 5 atm
u_G = 1.9 cm/sec
R_{Cn}/R_{C1}
1.00
0.80
0.60
0.40
0.20
0.10
T = 200°C
P_{CO} = 5 atm
P_{H_2} = 2 atm
u_G = 1.9 cm/sec
0 1 2 3 4 5 6 7 8 9 10 11
n - 1

Fig.2

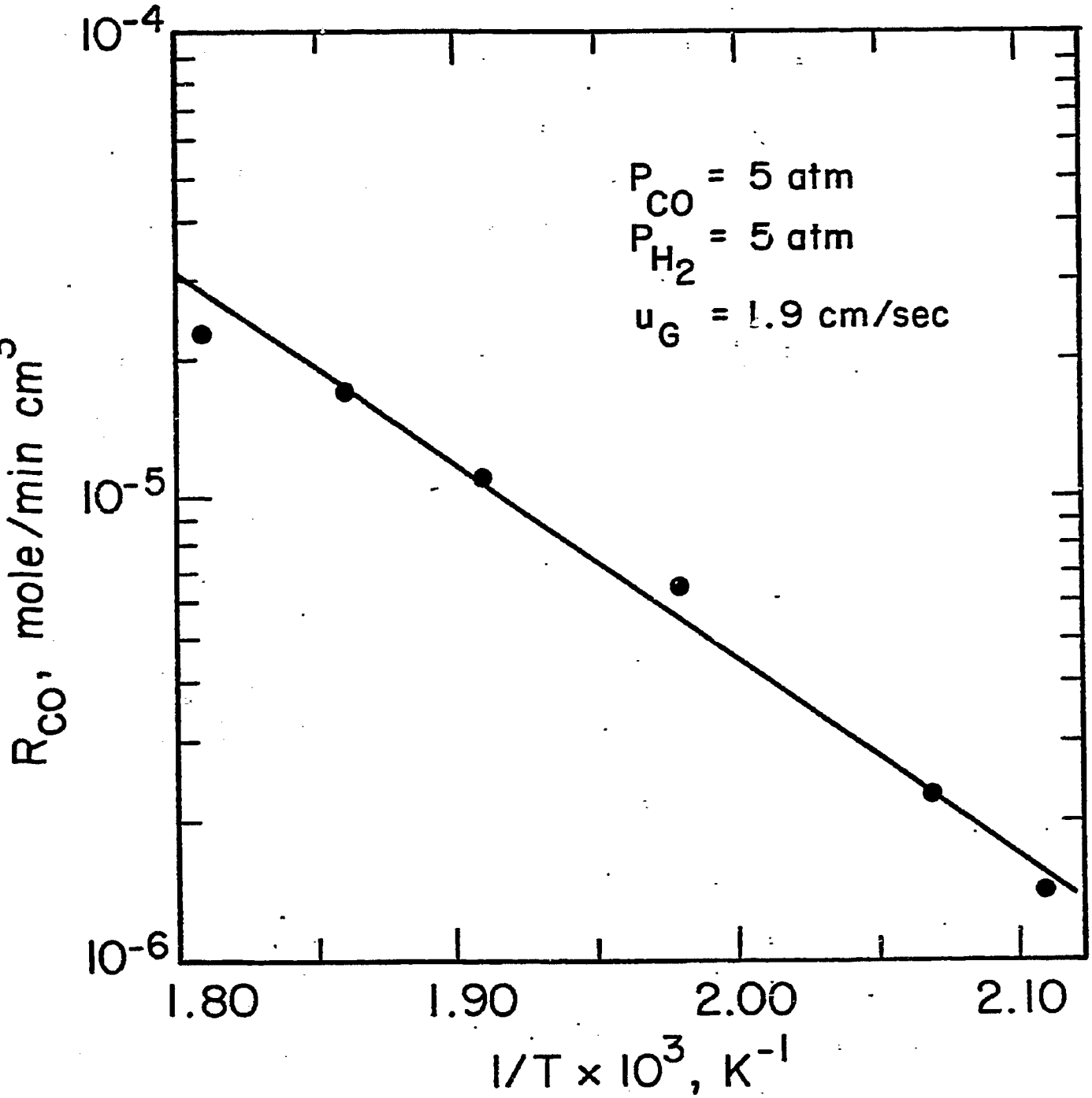
10^{-4}
10^{-5}
10^{-6}
R_{CO}, mole/min cm^3
P_{CO} = 5 atm
P_{H_2} = 5 atm
u_G = 1.9 cm/sec
1.80
1.90
2.00
2.10
$1/T \times 10^3$, K^{-1}

Fig. 3

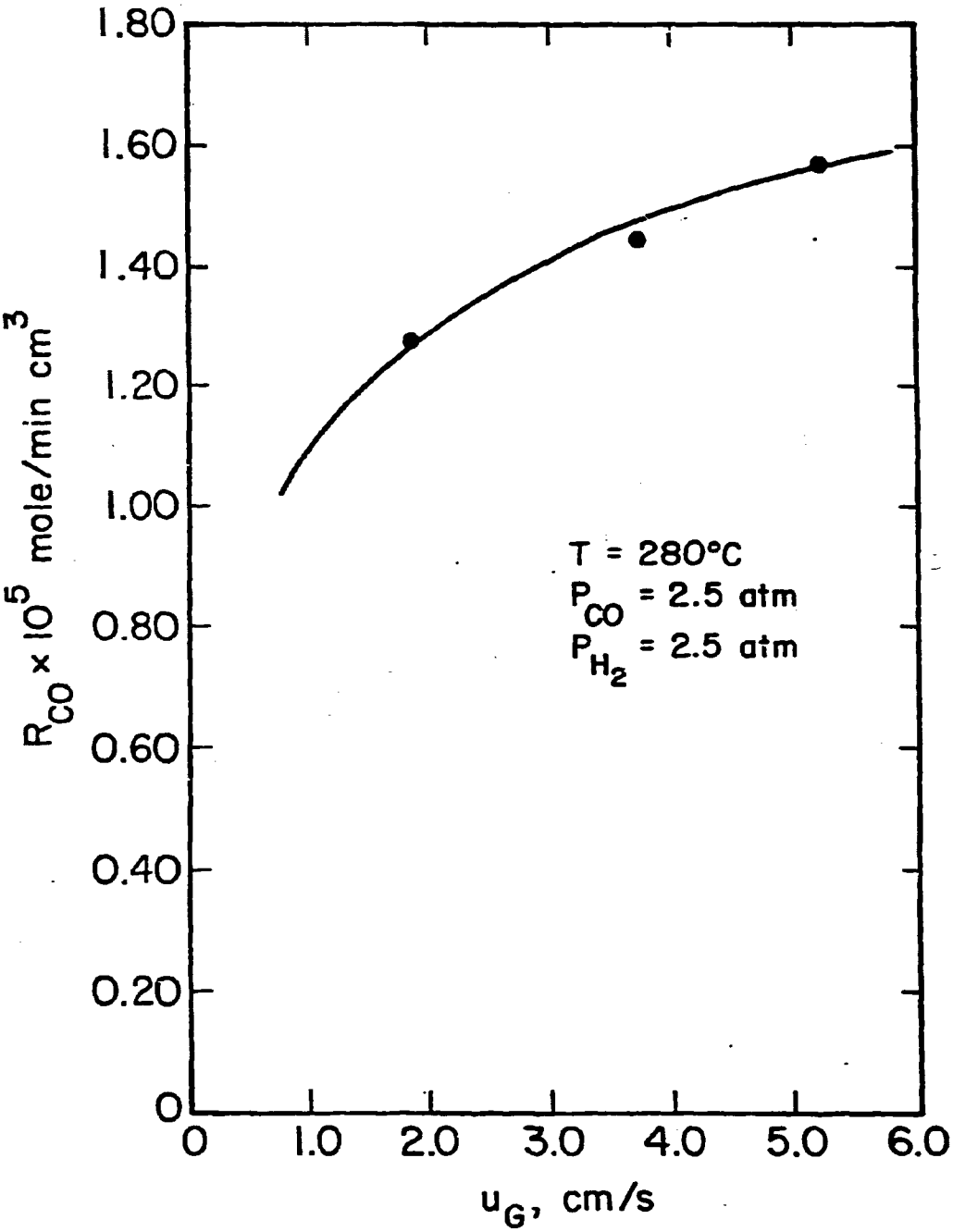
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0
0
1.0
2.0
3.0
4.0
5.0
6.0
$R_{CO} \times 10^5$ mole/min cm^3
u_G, cm/s
T = 280°C
P_{CO} = 2.5 atm
P_{H_2} = 2.5 atm

Fig. 4

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