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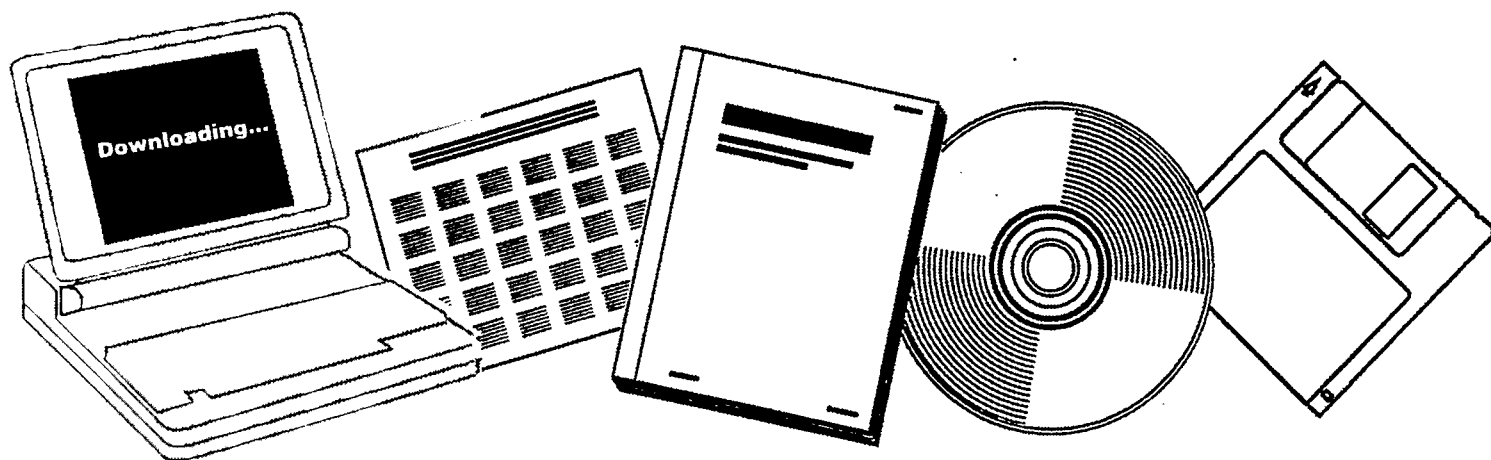
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SYNTHESIS GAS TO HYDROCARBONS. ANNUAL
REPORT, OCTOBER 1, 1981-SEPTEMBER 30, 1982**

CALIFORNIA UNIV., BERKELEY. DEPT. OF
CHEMICAL ENGINEERING

1982



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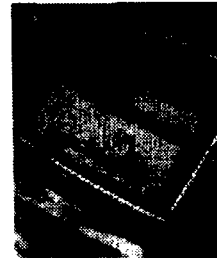
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DOE/PC/40795--T6

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MASTER

Conversion of Low H_2/CO Ratio
Synthesis Gas to Hydrocarbons

Grant #DE-FG22-81PC 40795

Annual Report
for the Period

October 1, 1981 to September 30, 1982

Submitted by

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ABSTRACT

The first goals of this project are: 1) to understand the influence of mass transfer on the performance of Fischer-Tropsch slurry reactors, and 2) to determine the nature of carbon formed during reaction. In reaching this second goal, knowledge of the catalyst composition will be useful.

Experiments aimed at the understanding of mass transfer effects have been initiated and are discussed in this report. Fischer-Tropsch synthesis has been carried out in a bubble-column slurry reactor (2.5 cm I.D.) filled with Parawax (C_{25+} paraffins). A fused-iron catalyst, promoted with potassium and copper, was used for all of the work reported here. The products were analyzed on line by gas chromatography.

Experiments have been performed at 250°C and 10 atm to determine the dependence of the synthesis rates on the partial pressures of H_2 and CO. Following a break in period, the catalyst activity remained constant over 4-day period of operation. For each set of partial pressures, a Schulz-Flory distribution of C_1 - C_{10} products was observed. The rate of formation of each product can be described by a power law expression of the form $r = k P_{H_2}^a P_{CO}^b$. The value of a is typically 0.9 to 1.0, in excellent agreement with what has been observed for experiments conducted in a well-stirred, slurry reactor using the same catalyst. A positive order CO dependence was observed, with the value of a increasing from 0.05 for CH_4 to 0.6 for C_4H_8 . These values are in sharp contrast with those found using the well-stirred reactor, where a is negative and increases from -0.4 for CH_4 to -0.2 for C_4H_8 .

The striking difference between the CO dependencies observed between the two reactors is believed to be due to the presence of severe mass-transfer effects in the bubble-column reactor. Our theoretical studies have shown that when liquid-phase mass-transfer limitations set in, the gradient in CO becomes more severe than in H_2 . This gives rise to a higher H_2/CO ratio at the catalyst surface. Studies conducted in the stirred-slurry reactor have shown that at H_2/CO ratios of 10 to 20 the rate of product synthesis becomes positive order in CO partial pressure. The validity of the present interpretation is currently being examined very carefully.

Introduction

Both experimental and theoretical work has been carried out during the past year to investigate mass transfer phenomenon in bubble column reactors. Experimental work was aimed at determining the extent to which mass transfer influences the performance of bubble column slurry reactors for the Fischer-Tropsch synthesis using potassium promoted fused iron catalysts suspended in another Parawax. Kinetic data measured at differential conversion in the bubble column slurry reactor are compared in this report with data measured under similar conditions in a stirred slurry reactor.

The theoretical work is aimed at developing a quantitative understanding of how axial mixing of gas, liquid, and catalyst influence the performance of bubble column slurry reactors.

Experimental Work

A bubble column reactor (1" I.D. x 72") was used. The reactor was filled with Parawax (C₂₅₊ paraffins) and a potassium and copper promoted fused iron catalyst was used in all experiments. Synthesis of hydrocarbons from CO and H₂ was studied at 250-270°C and 10 atm pressure. Products were analyzed by gas chromatography. A conventional well stirred reactor was used for the parallel experiments using the same catalyst and operating conditions.

Early experimental data in the slurry reactor (April 1 Progress Report) were obtained using a fouled frit. The pressure drop across the frit ranged from 15-50 psi during the course of an experiment. The pronounced mass transfer effects observed have probably been at least partially due to the partially plugged frit, resulting in a lower interfacial area. Data from these early runs are therefore largely disregarded.

After overcoming these experimental difficulties, the partial pressure dependence of synthesis rates was determined at 260°C and 250°C for hydrogen partial pressures ranging from 2 atm to 6 atm, and CO partial pressures ranging from 1 atm to 7 atm. The partial pressure dependence of the rates at 250°C was the same as that observed at 260°C, although the overall rate of CO consumption was higher by a factor of 1.9.

Results obtained at 260°C are shown in Figures 1-5. Figure 1 shows the rate of CO₂ production as a function of CO partial pressure, at a constant hydrogen partial pressure of 5 atm. The order with respect to CO is 0.58, compared to 0.57 measured in a previous run. Figure 2 shows the same plot for methane, ethylene, propene, butene, pentene, and hexene. As before, methane production shows negative order in dependence on CO, while the rates of production of heavier hydrocarbons show zero to positive order dependencies on CO partial pressure. Figure 3 shows the rates of hydrocarbon production as a function of hydrogen partial pressure at a constant CO partial pressure of 5 atm. As observed in previous experiments, the order with respect to H₂ is approximately 1, with a higher value observed for methane. Schulz-Flöry plots are shown as a function of hydrogen and

carbon monoxide partial pressures in Figure 4. As CO partial pressure increases, α increases, while an increase in H_2 partial pressure results in a decrease in α . Figure 5 shows the rate of CO_2 production as a function of H_2 partial pressure at 5 atm of CO. The order with respect to H_2 is 0.75. This value is considerably higher than the previously measured value of 0.41.

Discussion of Experimental Work

The reaction orders measured in the bubble column slurry reactor are compared to those measured in the well stirred slurry reactor in Table 1. For all products, the order with respect to CO is more positive in the bubble column than in the well stirred reactor. The reaction order with respect to H_2 in the two reactors does not differ except for the case of CO_2 .

The difference in hydrogen dependence of CO_2 production is believed to result from the presence of water in the CO. The water provides another source of oxygen which may act to produce a constant amount of CO_2 , regardless of the H_2 partial pressure. This could make the order with respect to H_2 appear lower when the CO is not purified. The experiments in the bubble column used CO that was dried with molecular sieve cooled with dry ice, while the stirred slurry experiments and previous bubble column experiments were carried out without purifying the CO.

The higher order with respect to CO may be explained as a mass transfer effect. As the mass transfer resistance becomes significant, the CO concentration at the catalyst surface drops, and the reaction becomes positive order in CO.

Theoretical work

The effects of axial mixing of gas, liquid, and catalyst can be assessed with the following model.

The gas phase mass balance for component i is written:

$$\frac{\epsilon}{Pe_g} \frac{d^2 \theta_{iG}}{d\zeta^2} - \frac{d(v\theta_{iG})}{d\zeta} - N_i(\theta_{iG} - \theta_{iL}) = 0$$

The overall balance, arrived at by summing the component balances, is given by:

$$\theta_G \frac{dv}{d\zeta} = - \sum_{i=1}^n N_i(\theta_{iG} - \theta_{iL})$$

The liquid phase mass balance for each component can be written

$$0 = \frac{1-\epsilon}{Pe_L} \frac{d^2 \theta_{iL}}{d\zeta^2} - \frac{d\theta_{iL}}{d\zeta} + N_{Li}(\theta_{iG} - \theta_{iL}) - v_1 Da_L \frac{m_1}{M_{w_2}} \theta_{H_2L}$$

Finally, the distribution of catalyst can be determined by solution of the following balance:

$$\frac{1}{Pe_S} \frac{d^2 C_S}{d\zeta^2} + \frac{dC_S}{d\zeta} = 0$$

The boundary conditions for these equations can be written:

At $\zeta = 0$

$$\theta_{iG}^o = \theta_{iG} \Big|_{\zeta=0} - \frac{\varepsilon}{Pe_g} \frac{d\theta_{iG}}{d\zeta} \Big|_{\zeta=0}$$

$$\theta_{iL}^o = \theta_{iL} \Big|_{\zeta=0} - \frac{1-\varepsilon}{Pe_L} \frac{d\theta_{iL}}{d\zeta} \Big|_{\zeta=0}$$

$$U_L C_S^o = (U_L - v_p) C_S \Big|_{\zeta=0} - \frac{E_p}{L} \frac{dC_S}{d\zeta} \Big|_{\zeta=0}$$

At $\zeta = 1$

$$\frac{d\theta_{iG}}{d\zeta} = 0$$

$$\frac{d\theta_{iL}}{d\zeta} = 0$$

Finally,

$$\int_0^1 C_S d\zeta = 1$$

These equations are boundary value equations, whose solutions can readily be approximated via orthogonal collocation. The subroutine "COLSYS", available on the CDC 7600 at LBL, will be used to solve the mass balances, and generate concentration profiles for each phase.

Plans For The Oming Year

We plan to accumulate data on the performance of our bubble-column reactor over a broad range of operating conditions, and to compare the results with rates and products structures obtained in a well-stirred slurry reactor. We will improve our current theoretical model of the bubbles-column reactor to include the effects of gas, liquid, and catalyst dispersion, as well as improved estimates of reactant and product mass-transfer coefficients. The model will then be used to examine the antici-

pated performance of laboratory, pilot-plant, and full-scale reactors over a broad range of operating conditions. Upon completion of these studies, we will initiate efforts to determine the kinetics of carbon formation and loss in a slurry reactor. We will also examine the possibility of using zeolite-impregnated iron catalysts, prepared in such a fashion as to minimize graphite formation within the zeolite or on its exterior surface.

NOMENCLATURE

- a - Bubble interfacial area per unit reactor volume (cm^{-1})
 $C_{G,i}$ - Gas-phase concentration of component i (mol/cm^3)
 $C_{L,i}$ - Liquid-phase concentration of component i (mol/cm^3)
 C_S - Dimensionless catalyst concentration, w/\bar{w}
 Da_L - Damkohler number, $\frac{Lk_o}{U_L}$
 E_g, E_L, E_S - Gas, liquid, and solid dispersion coefficients, cm^2/sec
 k_o - Rate coefficient ($\text{cm}^3/\text{g s}$)
 $k_{L,i}$ - Liquid-phase mass-transfer coefficient for component i (cm^2/s)
 L - Reactor length (cm)
 m_i - Solubility coefficient for component i
 N_i - Stanton number for component i ,
 $N_{L,i}$ - Liquid Stanton number, $\frac{k_{L,i} a L}{U_L}$
 Pe_g - Liquid phase Pellet number, $\frac{U_L L}{E_L}$
 Pe_L - Liquid phase Pellet number, $\frac{U_L L}{E_L}$
 Pe_S - Solid Pellet number, $\frac{(U_L - v_S)L}{E_S}$
 Q_L - Liquid-phase flow rate (cm^3/s)
 r_i - Rate of formation or consumption of component i ($\text{mol}/\text{g s}$)
 U_G - Superficial gas velocity (cm/s)

- U_L - Liquid superficial velocity, cm/sec
- V_R - Reactor volume (cm^3)
- V_S - Settling velocity of solids, cm/sec
- w - Catalyst loading (g/cm^3 of slurry)
- \bar{w} - Average catalyst concentration, g/cm^3 slurry
- z - Distance from the gas inlet (cm)
- ϵ_G - Fraction of the total reactor volume occupied by bubbles
- θ_G - Dimensionless gas-phase concentration
- $\theta_{G,i}$ - Dimensionless gas-phase concentration of component i ,
- $\theta_{L,i}$ - Dimensionless liquid-phase concentration of component i ,
- ν_i - Stoichiometric coefficient for component i
- ρ_L - Liquid density (g/cm^3)
- τ_G - Gas space time (s)
- τ_L - Liquid space time (s)
- v - Dimensionless gas velocity, U_G/U_G^0

Table 1

KINETIC MEASUREMENTS

$$R = kP_{CO}^a P_{H_2}^b$$

	STIRRED SLURRY	BUBBLE COLUMN SLURRY
CO ₂	a = 0.36 b = 0.38	a = 0.58 b = 0.75
CH ₄	a = -0.42 b = 1.11	a = -0.23 b = 1.14
C ₂ + C ₆	a = -0.2 + 0.0 b = 1.0 + 1.1	a = 0 + 0.20 b = 1.0 + 1.1

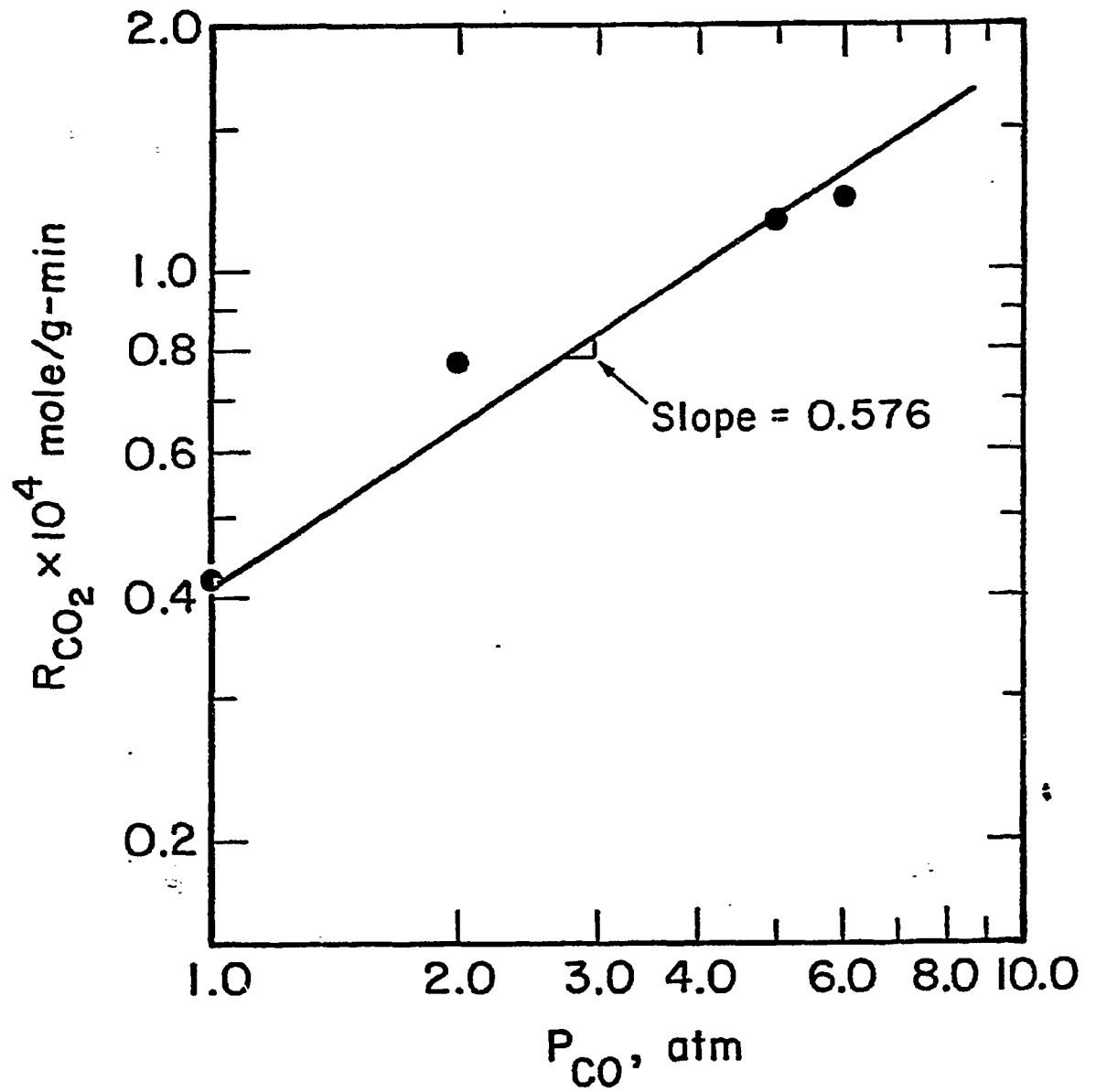


Figure 1

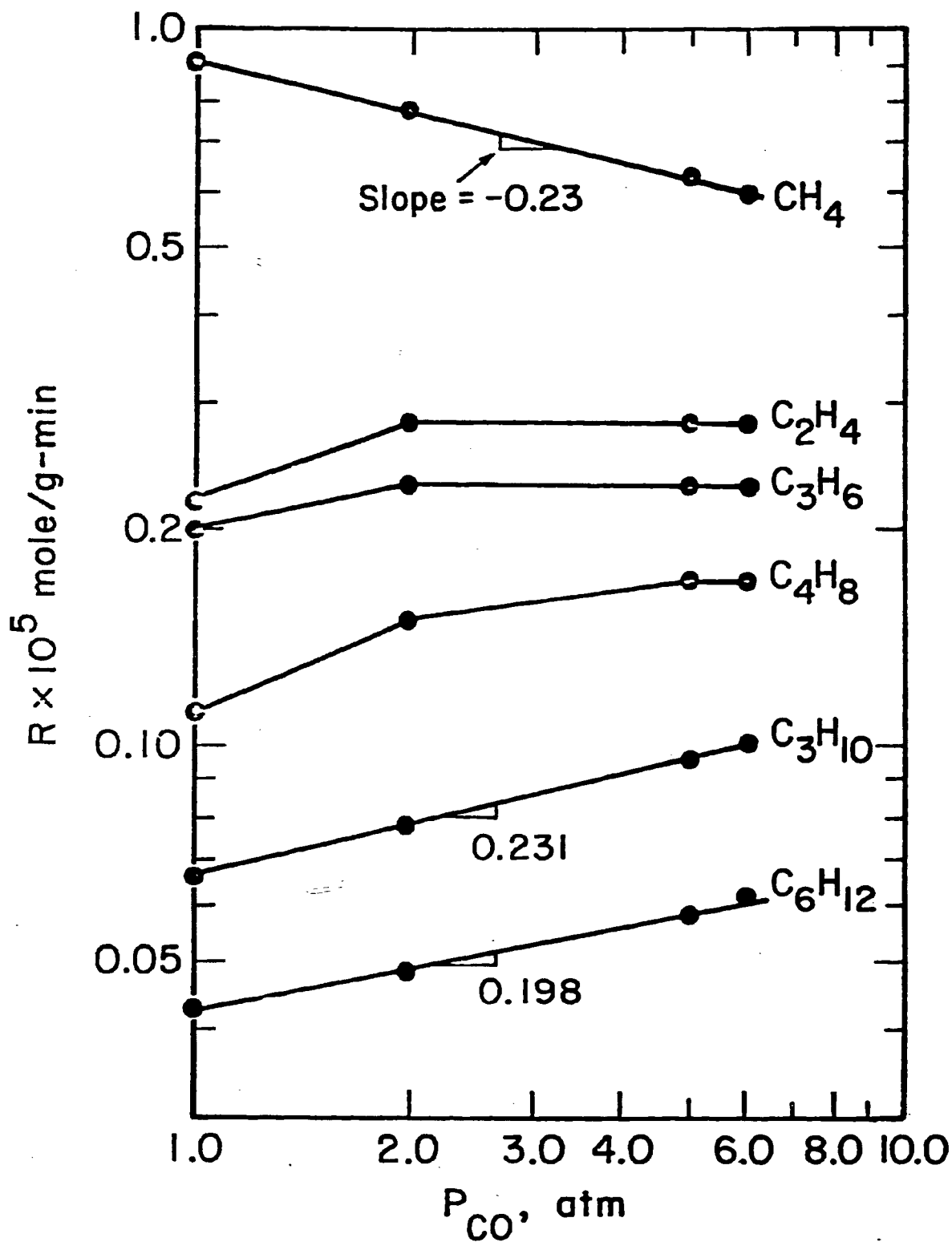


Figure 2

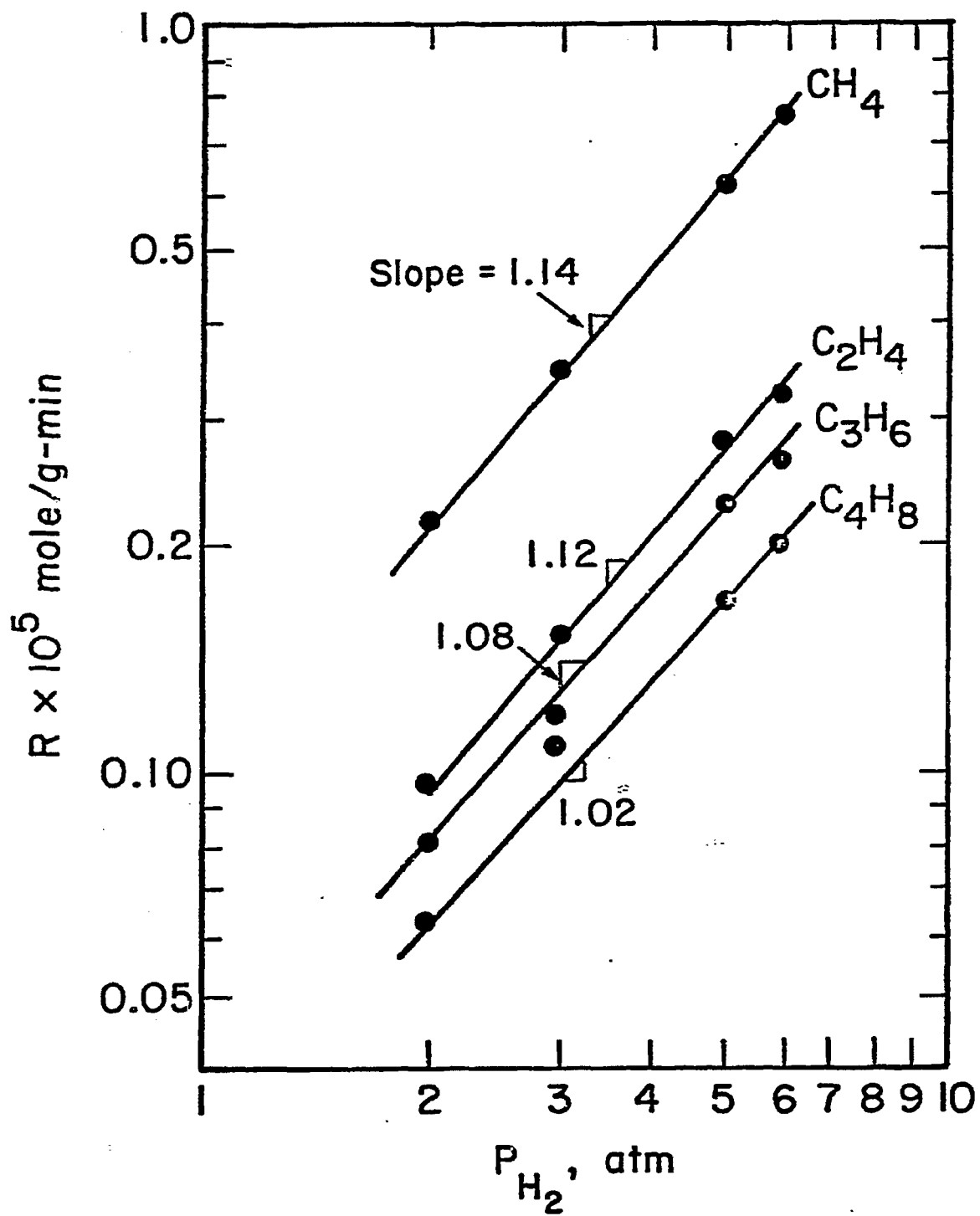


Figure 3

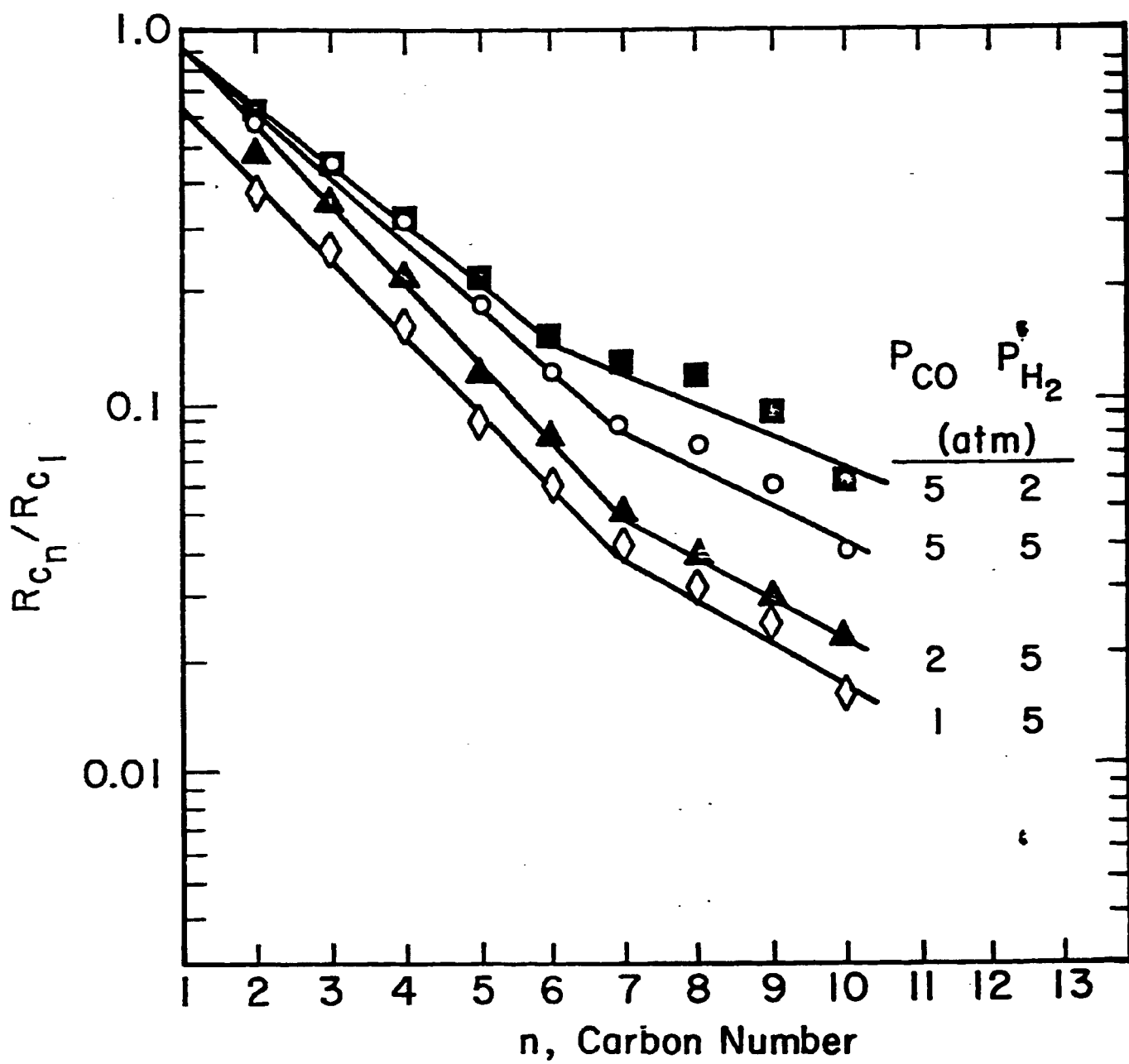


Figure 4

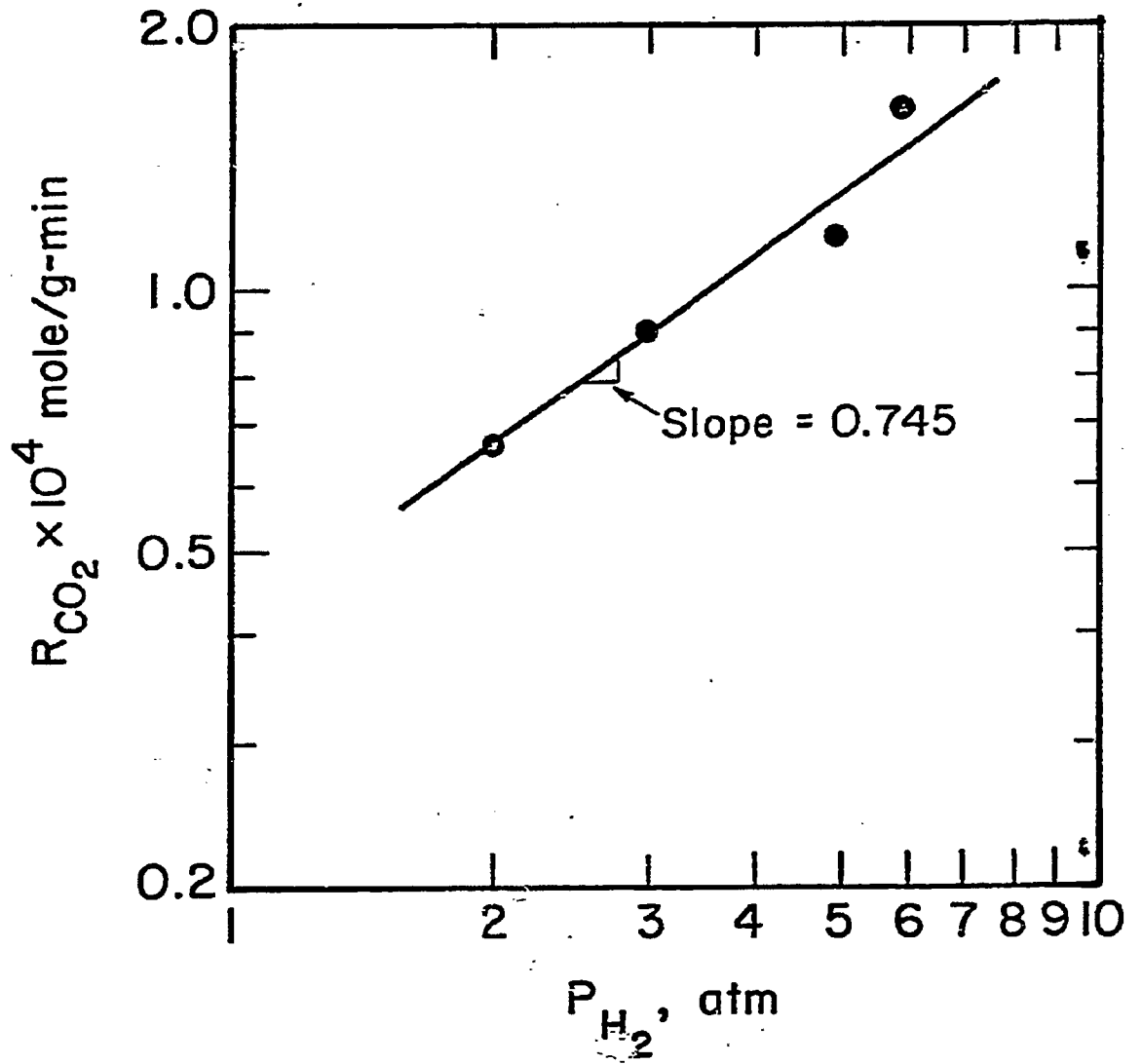


Figure 5

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