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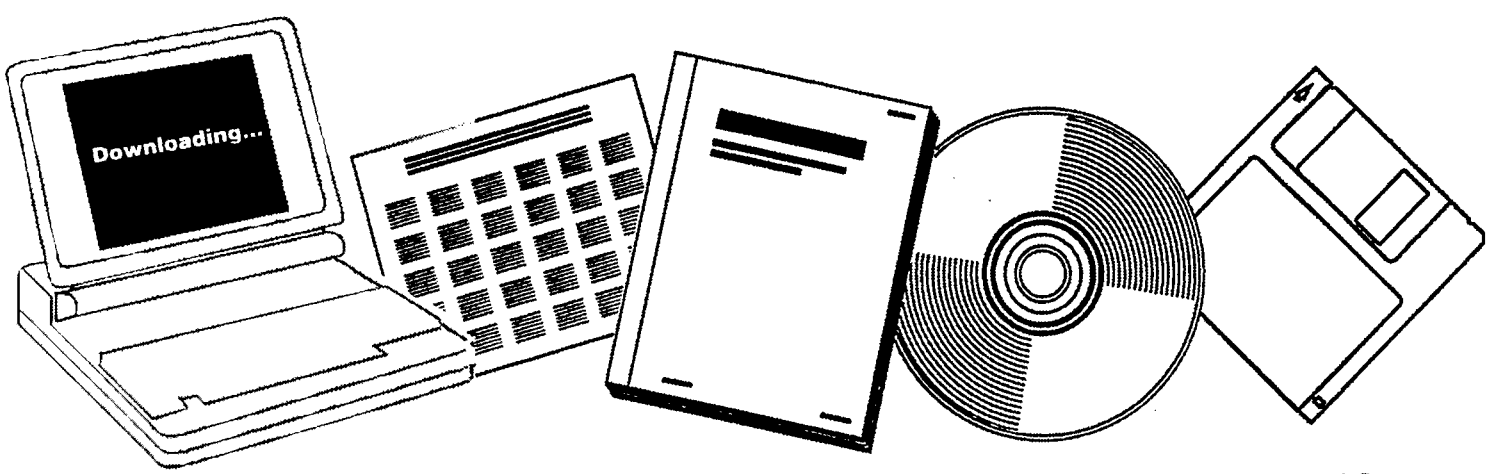
CONVERSION OF LOW H SUB 2 /CO RATIO SYNTHESIS GAS TO HYDROCARBONS. PROGRESS REPORT OCTOBER 1, 1982-DECEMBER 31, 1982

CALIFORNIA UNIV., BERKELEY. DEPT. OF CHEMICAL ENGINEERING

1986



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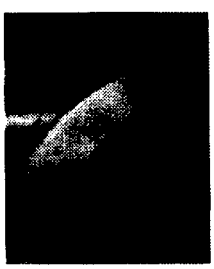

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Conversion of Low H_2/CO Ratio Synthesis Gas to Hydrocarbons

Grant No. DE-FG22-81PC40795

MASTER

Progress Report
for the Period

October 1, 1982 to December 31, 1982

Submitted by

Alexis T. Bell
Heinz Heinemann

Department of Chemical Engineering
University of California, Berkeley, California 94720

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ABSTRACT

Further experiments were carried out to see if mass-transfer resistances in the Fischer-Tropsch slurry reactor influence the rate of the synthesis reaction. The results indicate that, with the fused iron catalyst currently being used, mass transfer resistances have no effect on the rate.

The data obtained enable us to examine the effects of temperature, pressure, and catalyst pretreatment on the rate of carbon formation in the slurry reactor. The rate of carbon formation relative to hydrocarbon formation is a strong function of the degree of reduction of the catalyst, but shows no dependence on total pressure or temperature.

Calculations were carried out to assess the influence of column diameter on mixing and H_2/CO ratios in the slurry. It was found that for a reactor 10 cm in diameter, the reactor behaves as if the liquid and gas are unmixed, while a reactor of diameter 75 cm shows well-stirred behavior in both phases.

Experimental

In the previous report, we compared rate expression measured in a stirred slurry reactor to those measured in a bubble-column slurry reactor. The order with respect to CO was slightly higher in the bubble column than in the stirred slurry reactor. This difference was thought to result from the high resistance to CO mass transfer, which lowers the CO concentration at the catalyst surface and moves the kinetics into a more positive order regime.

Calculations based on the best available values for k_La indicate that mass transfer resistances would not significantly influence the CO concentration at the catalyst surface. This contradiction between experiments and calculations led us to carry out experiments with hexane, iron catalysts, and nitrogen in a glass column. Large bubbles were (1-2 cm) observed. Thus, it seemed that the presence of large bubbles accounted for a high mass transfer resistance for CO that could explain our data. The experiments performed this quarter were aimed at verifying a large resistance to mass transfer. The rate of reaction at different levels of activity (as influenced by temperature and degree of reduction) were measured as a function of gas flow rate at $P_T = 5$ atm and $H_2/CO = 1$. Flow rates varied from 1800 to 500 NCCM. At all levels of activity, the rates of reaction of both methane and CO_2 were not influenced by the gas flow rate. Since the rate of CO_2 formation has a relatively high partial pressure, dependence on CO ($R_{CO_2} \sim kP_{CO}^{0.5}$), its production rate would be strongly influenced by any changes in CO concentration. Methane, on the other hand, shows a strong dependence on hydrogen partial pressure ($R_{CO_4} \sim kP_{H_2}^{1.2}$), and its production rate wold be sensitive to changes in H_2 concentration.

The fact that the production rates of both CO_2 and CH_4 do not depend on the gas flowrate indicates that mass transfer resistances for both CO and H_2

are small. Consequently, the observed differences in partial pressure dependencies for the two reactors probably result from some difference in catalyst pretreatment.

The kinetic data generated can be used to examine the kinetics of the Fischer-Tropsch synthesis. In particular, the rate of carbon formation can be estimated as a function of temperature, pressure, and degree of reduction. The rate of consumption of CO to produce hydrocarbons is given by:

$$R_{HC} = \sum_{n=1}^{\infty} nR_n$$

The rate of rejection of oxygen as CO_2 is given by R_{CO_2} if none of the oxygen is rejected as H_2O, and no carbon (or carbide) formation occurs. In this case $R_{HC} = R_{CO_2}$. If some oxygen is rejected as H_2O, and no carbon is formed, $R_{HC} > R_{CO_2}$. If some CO is converted to carbon (or carbide), $R_{HC} < R_{CO_2}$.

Preliminary calculations based on the experiments completed this quarter allow the following conclusions to be made:

1. (a) Iron catalyst that has been reduced for 24 hrs in H_2 at 300°C following 24 hrs of treatment with H_2 and CO at 300°C does not convert much CO to carbon (carbide) at either 250 or 300°C ($R_{CO_2} \simeq \sum_{n=1}^{6} nR_n$).

   (b) The rates CO_2 production and total hydrocarbon production remain in balance at 250°C, irrespective of total pressure.

2. After reducing the above catalyst for an additional 24 hrs in H_2 at 300°C, the rate of carbon production increases dramatically, relative to the rate of hydrocarbon production i.e., $R_{CO_2} = 1.7 \sum_{n=1}^{6} nR_n$. This is true both at 300°C and 250°C.

It should be noted that hydrocarbons of carbon number higher than six have not been included in these calculations. Detailed calculations using carbon numbers 1 through 10 will allow more definitive conclusions.

Future Work

The carbon formation rate has been measured as a function of partial pressures in an earlier set of experiments, but the effect of temperature is not well understood. Future work will involve a detailed analysis of the data already obtained, and the measurement of carbon formation rate as a function of temperature. In addition, the degree of reduction of the catalyst has a strong influence on the rate of carbon formation. This may be worth pursuing further.

Since mass transfer effects cannot be observed with the present catalyst, a more active catalyst, probably Ru/Al_2O_3, will be employed.

Theoretical

In the last report, a model that accounts for axial mixing in both phases was developed. The equations have been solved for three cases, and the resulting concentration profiles are shown in Figures 1, 2, and 3. Figure 1 shows the concentration profiles generated for a column 10 cm in diameter, with mass transfer and kinetic parameters identical to those used in our previous work. These profiles are significantly different from those generated by assuming a well-mixed liquid and an unmixed gas, which are shown in Figure 4. The two major differences between the two sets of profiles are as follows:

1. The "axial mixing" model predicts that the gas phase H_2 and CO concentrations are nearly equal, while the well stirred liquid model predicts widely differing values for gas phase H_2 and CO concentrations.

2. The $(H_2/CO)_L$ ratio in the "axial mixing" case is significantly higher than that predicted by the well-mixed liquid model.

Both differences result from lower degree of liquid mixing in the model shown in Figure 1. This can be seen by examining the balances for completely unmixed gas and liquid phases. The liquid phase mass balances becomes:

$$k_{L,i}a\left[\frac{C_{G,i}}{m_i} - C_{L,i}\right] = \nu_i k^o C_{L,H_2} ,$$

while the gas phase mass balance becomes:

$$-\frac{d(uC_{G,i})}{dz} = k_i a\left[\frac{C_{G,i}}{m_i} - C_{L,i}\right] = \nu_i k_R C_{L,H_2}$$

$$\sum_{i=1}^{n} \nu_i k^o C_{L,H_2} = -C_G \frac{du}{dz}$$

The concentration profile for hydrogen can be calculated directly from these three equations. The gas phase concentrations of the remaining components are determined by the stoichiometry of the reaction. For the assumed stoichiometry, $C_{G,H_2} = C_{G,CO}$. Thus, any difference in mass transfer driving force for CO and H_2 must result from differences in liquid concentrations, and an unmixed liquid results in an elevated H_2/CO ratio. The profiles shown in Figure 1 are characteristic of an unmixed slurry phase.

In Figures 2 and 3, the effect of column diameter is shown. Figure 2 shows the "unmixed" case, for a 10 cm in diameter column, while Figure 3 shows profiles for a column 75 cm in diameter. The Peclet numbers for both phases are lower and concentration profiles are flatter. The increased mixing decreases both the H_2/CO ratio and the conversion of CO.

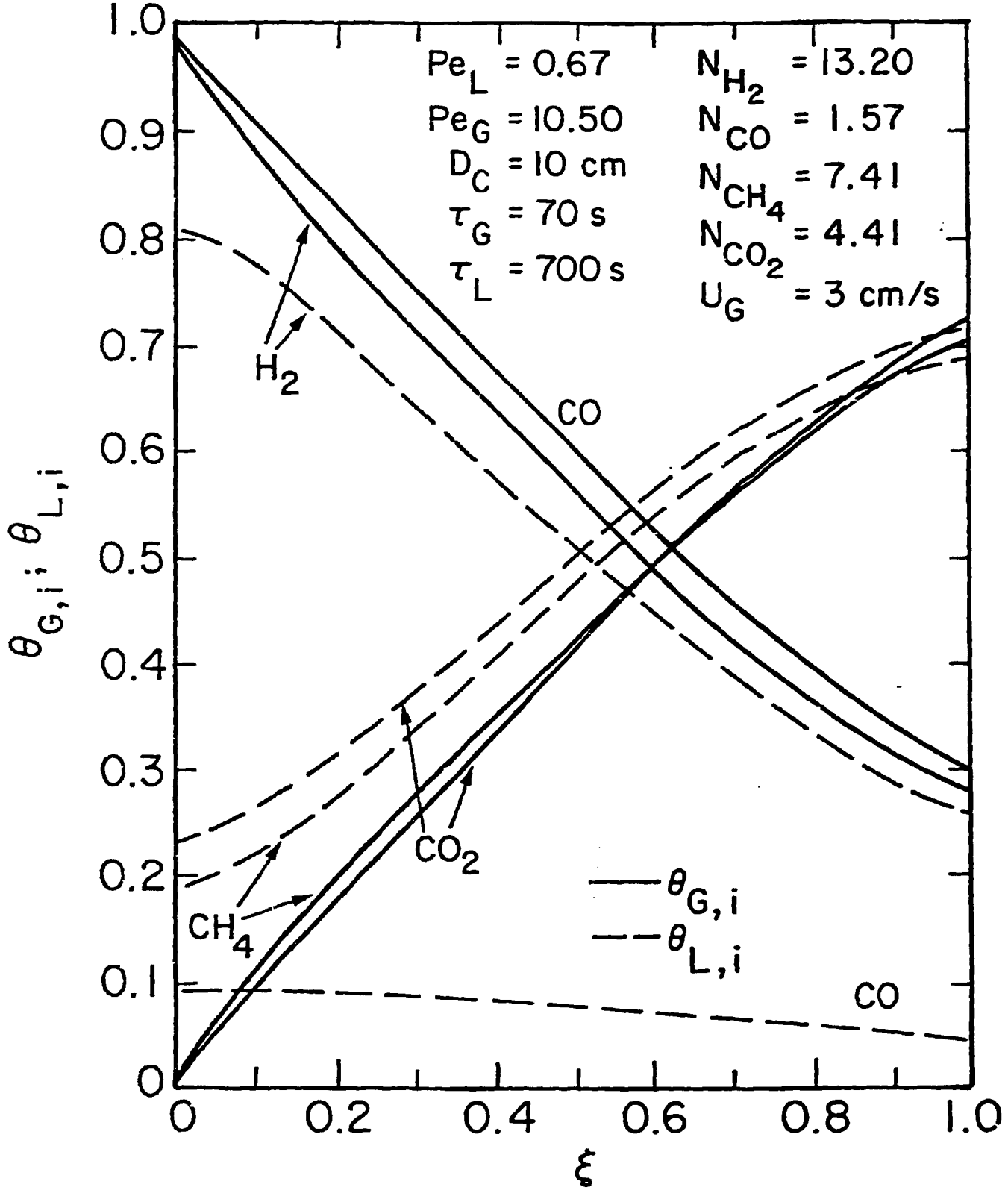
Future Work

Small diameter columns may exhibit behavior characteristic of unmixed liquid and gas phases, while large diameter reactors show well mixed behavior in both phases. The degree of mixing can have a strong influence on H_2/CO ratio and conversion. Thus, the effects of reactor diameter can be important, and should be accounted for in scale-up. Future calculations will be aimed at understanding the effects of design parameters (diameter, length, velocity, catalyst loading), and at understanding the precision to which mass transfer and mixing parameters must be known to accurately predict the behavior of Fischer-Tropsch slurry reactors.

Conclusions

The rate of reaction using the current fused iron catalyst is not influenced by mass transfer resistances. The rate of carbon formation relative to hydrocarbon formation depends strongly on the catalyst pre-treatment, but not on the temperature or total pressure.

Calculations show that in small diameter reactors, significant deviation from complete mixing in the liquid phase may be expected, while large diameter reactors will exhibit well-stirred behavior in both phases.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Pe_G = 10.50
D_C = 10 cm
τ_G = 70 s
τ_L = 700 s
N_{H_2} = 13.20
N_{CO} = 1.57
N_{CH_4} = 7.41
N_{CO_2} = 4.41
U_G = 3 cm/s
H_2
CO
CO_2
CH_4
CO
$\theta_{G,i}$
$\theta_{L,i}$
$\theta_{G,i}$; $\theta_{L,i}$
ξ
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
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0.9
1.0
0.2
0.4
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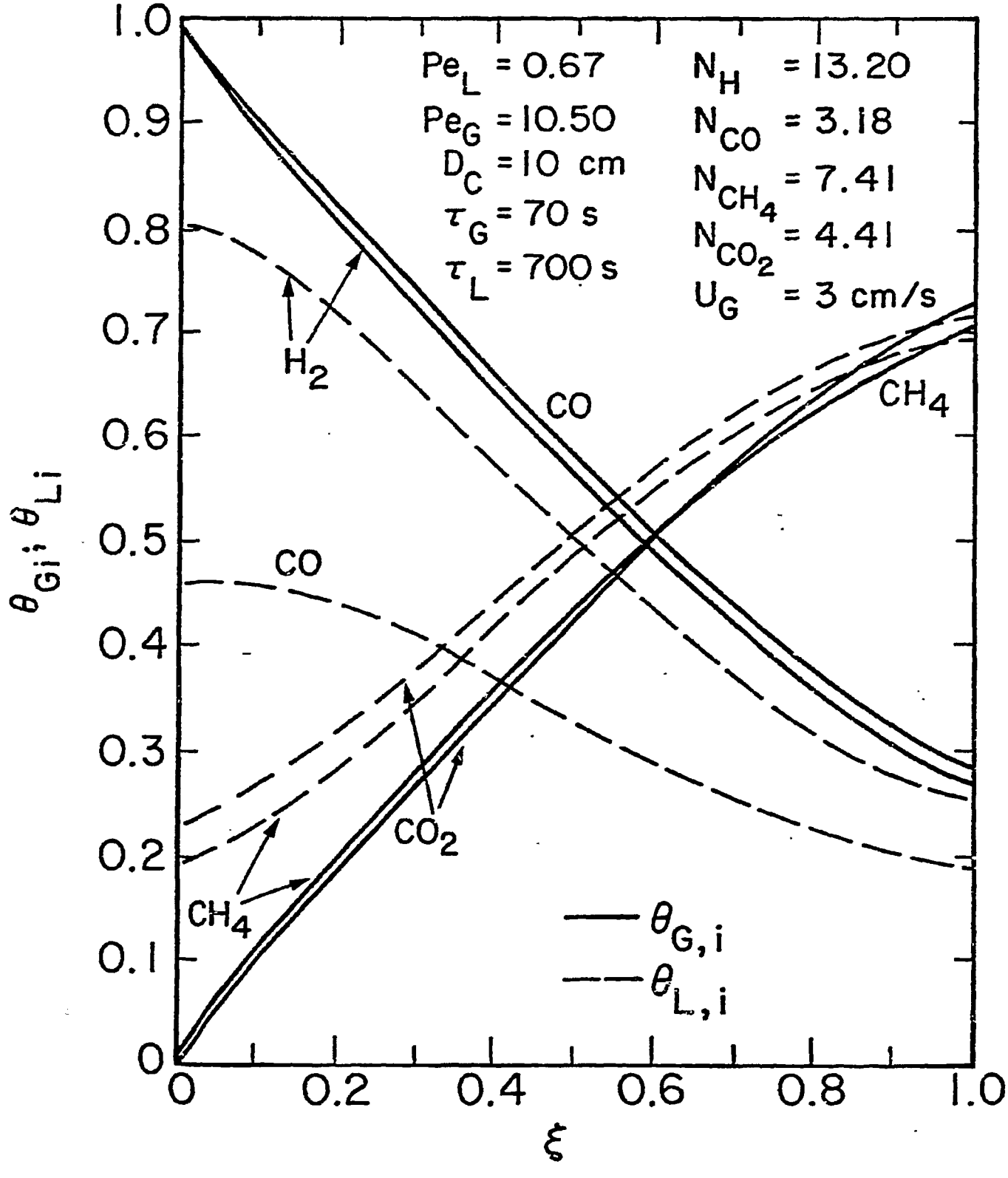
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Pe_G = 10.50
D_C = 10 cm
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τ_L = 700 s
N_H = 13.20
N_{CO} = 3.18
N_{CH_4} = 7.41
N_{CO_2} = 4.41
U_G = 3 cm/s
H_2
CO
CH_4
CO
CO_2
CH_4
$\theta_{G,i}$
$\theta_{L,i}$
$\theta_{Gi}; \theta_{Li}$
ξ
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
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0.4
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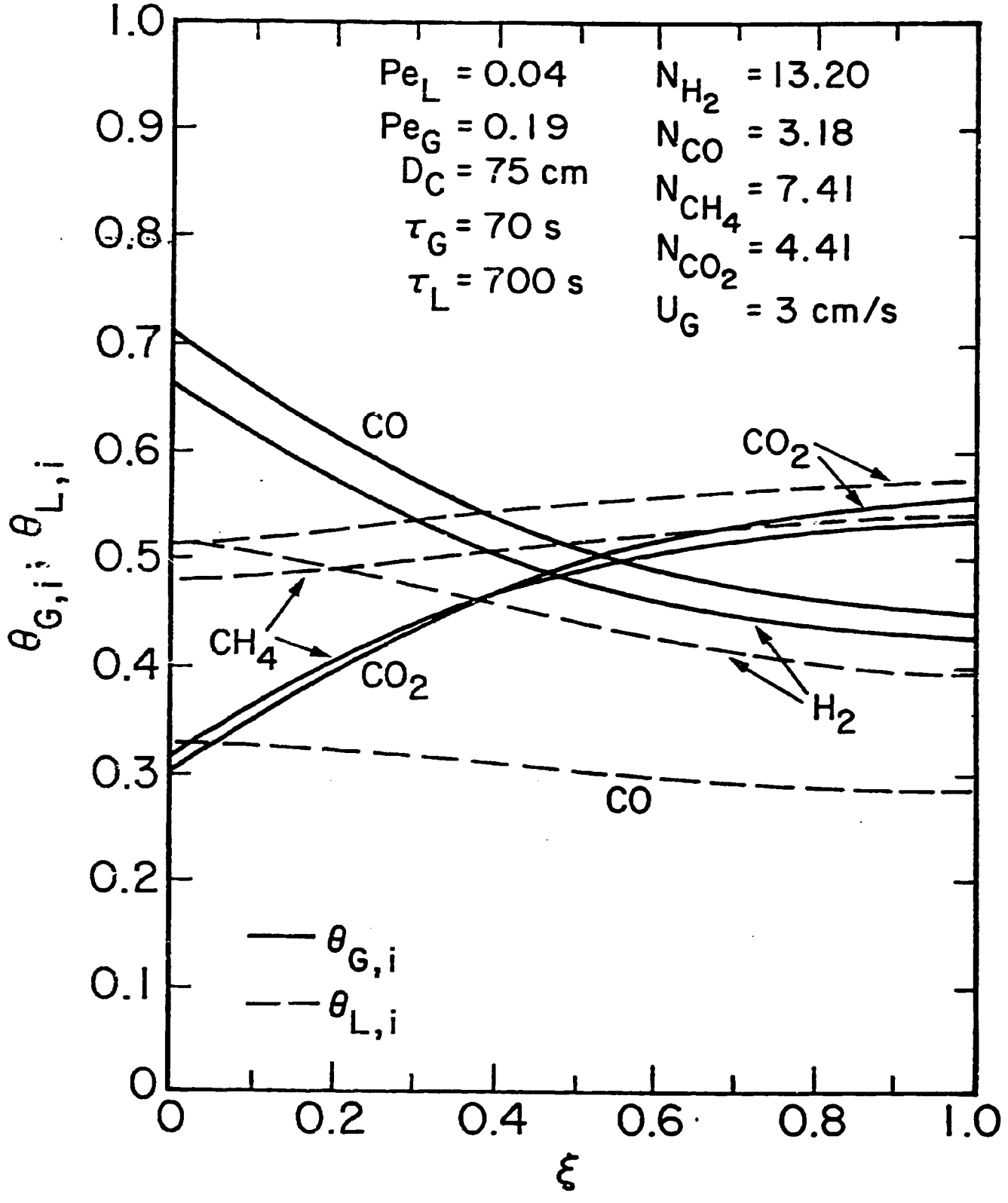
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D_C = 75 cm
τ_G = 70 s
τ_L = 700 s
N_{H_2} = 13.20
N_{CO} = 3.18
N_{CH_4} = 7.41
N_{CO_2} = 4.41
U_G = 3 cm/s
CO
CO_2
CH_4
CO_2
H_2
CO
$\theta_{G,i}$
$\theta_{L,i}$
$\theta_{G,i}$; $\theta_{L,i}$
ξ
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
0.2
0.4
0.6
0.8
1.0

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