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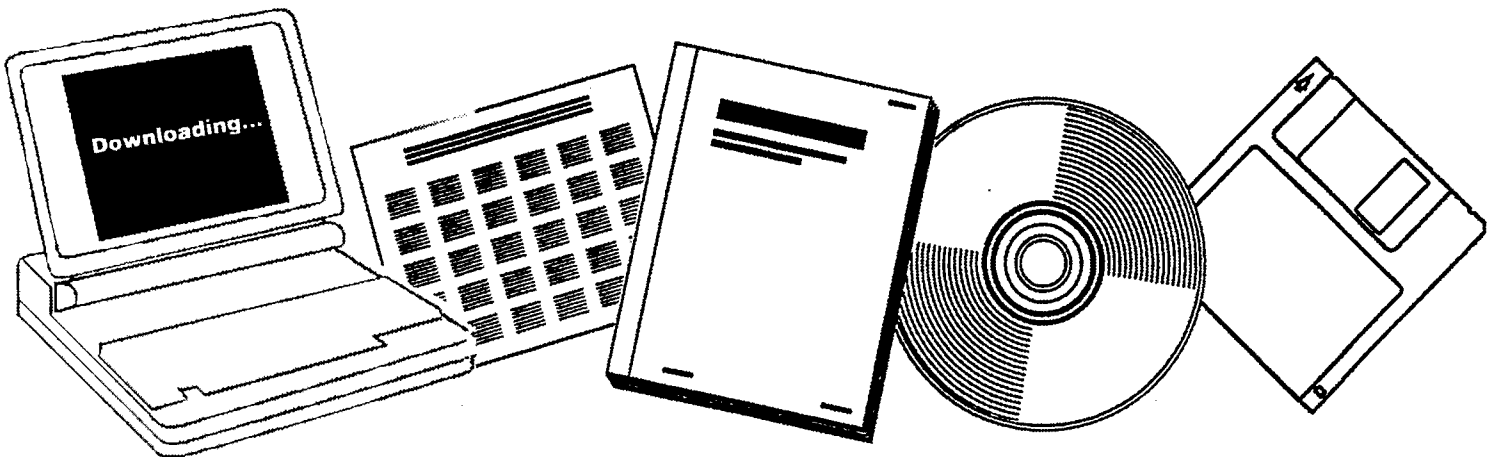
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**CONVERSION OF LOW H SUB 2 /CO RATIO  
SYNTHESIS GAS TO HYDROCARBONS: FINAL  
REPORT, OCTOBER 1, 1981-SEPTEMBER 30, 1986**

**CALIFORNIA UNIV., BERKELEY. DEPT. OF  
CHEMICAL ENGINEERING**

1986



U.S. Department of Commerce  
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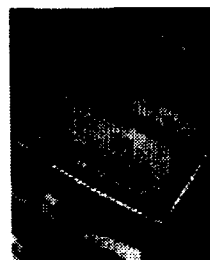
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Final Report

Conversion of Low  $H_2/CO$  Ratio  
Synthesis Gas to Hydrocarbons

DOE Project DE-FG22-81PC40795

October 1, 1981 - September 30, 1986

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## BACKGROUND AND PROJECT OBJECTIVES

Slurry or bubble-column reactors offer two main advantages over fixed fluidized bed reactors for carrying out Fischer-Tropsch synthesis of hydrocarbons. First, bubble-column reactors can process a low  $H_2/CO$  ratio synthesis gas without reactor plugging or catalyst deactivation due to carbon formation. Second, agitation of the slurry by rising gas bubbles provides good heat transfer to the reactor walls, thereby minimizing temperature gradients and eliminating hot spots which can cause rapid catalyst deactivation.

The objectives of this project have been twofold: 1) to develop a theoretical model for designing bubble-column reactors and assessing their performance and 2) to characterize the performance of a laboratory-scale bubble-column reactor. The theoretical part of the project has focused the effects of gas-liquid mass transfer; axial dispersion of gas, liquid, and catalyst; and the interplay between the kinetics of Fischer-Tropsch synthesis and the water-gas-shift reaction. The experimental portion of the project has focused the effects of reaction conditions on product distribution and, in particular, the conditions under which gas-liquid mass transfer becomes important. Any independent set of experiments was undertaken to investigate the chemistry of carbonaceous deposits formed during Fischer-Tropsch synthesis.

## PROJECT ACCOMPLISHMENTS

### Theoretical Studies

A major accomplishment of this project has been the development of a comprehensive model for describing bubble-column performance. This model assumes that the reactor is isothermal and that there are no radial gradients in the concentrations of reactants or products. Both assumptions are supported by previous experimental work (1).

The model is written in terms of the following dimensionless variables:

$$\theta_{G,i} = \frac{C_{G,i}}{C_{G,H_2}^0}, \quad \theta_{L,i} = \frac{C_{L,i} m_i}{C_{G,H_2}^0}, \quad \theta_G = \frac{C_G}{C_{G,H_2}^0} \quad (1)$$

$$w = \frac{w}{w_0}, \quad v = \frac{U_G}{U_G^0}, \quad \zeta = \frac{z}{L}$$

The dimensionless groups appearing in the mass balances are

$$N_{G,i} = \frac{k_{L,i} a L}{m_i U_G^0}, \quad N_{L,i} = \frac{k_{L,i} a L}{U_L}$$

$$Pe_G = \frac{U_G^0 L}{D_G}, \quad Pe_L = \frac{U_L L}{D_L}, \quad (2)$$

$$Pe_s = \frac{(U_S - U_L/\epsilon_L)L}{D_s}.$$

Definitions of the variables, coefficients, and dimensionless groups appearing in eqns. 1 and 2, and in subsequent equations, are given in the Notation.

The gas-phase mass balance for component  $i$  is written:

$$\frac{\epsilon_G}{Pe_G} \frac{d^2 \theta_{G,i}}{d\zeta^2} - \frac{d(u\theta_{G,i})}{d\zeta} - N_{G,i}(\theta_{G,i} - \theta_{L,i}) = 0. \quad (3)$$

The boundary conditions on eq. (3) are:

$$\theta_{G,i} - Pe_G^{-1} \frac{d\theta_{G,i}}{d\zeta} = \theta_{G,i}^0 \quad \text{at } \zeta = 0. \quad (4)$$

$$\frac{d\theta_{G,i}}{d\zeta} = 0 \quad \text{at } \zeta = 1. \quad (5)$$

To determine  $u$ , it is necessary to write an overall mass balance. This is done by summing the component balances and noting that the total gas-phase concentration is independent of position in the reactor. Thus,

$$\epsilon_G \frac{du}{d\zeta} - \sum_i N_{G,i}(\theta_{G,i} - \theta_{L,i}) = 0. \quad (6)$$

The boundary condition on eq. (6) is:

$$u = 1 \quad \text{at } \zeta = 0. \quad (7)$$

The liquid-phase mass balance for each component is given by:

$$\frac{\epsilon_L}{Pe_L} \frac{d^2 \theta_{L,i}}{d\zeta^2} - \frac{d(\theta_{L,i})}{d\zeta} + N_{L,i} (\theta_{G,i} - \theta_{L,i}) + \rho_i = 0. \quad (8)$$

The appropriate boundary conditions for eq. (8) are:

$$\theta_{L,i} - \frac{\epsilon_L}{Pe_L} \frac{d\theta_{L,i}}{d\zeta} = \theta_{L,i}^0 \quad \text{at } \zeta = 0. \quad (9)$$

$$\frac{d\theta_{G,i}}{d\zeta} = 0 \quad \text{at } \zeta = 1. \quad (10)$$

The axial distribution of catalyst is governed by gravitational settling and axial dispersion due to agitation of the catalyst slurry by the gas flow. Assuming that the volume fraction of liquid is essentially constant along the column length, the mass balance on catalyst can be written:

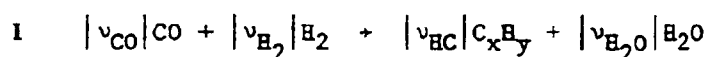
$$Pe_s^{-1} \frac{d^2 \omega}{d\zeta^2} + \frac{d\omega}{d\zeta} = 0. \quad (11)$$

The boundary conditions on eq. 11 are:

$$\omega - Pe_s^{-1} \frac{d\omega}{d\zeta} = 0 \quad \text{at } \zeta = 0 \quad (12)$$

$$\int_0^1 \omega d\zeta = 1. \quad (13)$$

Hydrocarbons and water are the primary products of the Fischer-Tropsch synthesis over iron catalysts. As a consequence, the overall reaction stoichiometry can be represented as



The values of  $v_i$ ,  $x$ , and  $y$  depend on the probability of chain growth,  $\alpha$ , and the overall fraction of  $C_2^+$  paraffins,  $\gamma$ . Thus,

$$v_{CO} = \frac{-1}{5 + (1-\alpha)^2 + \gamma\alpha(1-\alpha)}$$

$$v_{H_2} = \frac{2 + (1-\alpha)^2 + \gamma\alpha(1-\alpha)}{3 + (1-\alpha)^2 + \gamma\alpha(1-\alpha)}$$

(14)

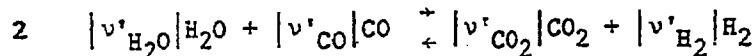
$$v_{H_2O} = \frac{-1}{3 + (1-\alpha)^2 + \gamma\alpha(1-\alpha)}$$

$$v_{HC} = \frac{(1-\alpha)}{3 + (1-\alpha)^2 + \gamma\alpha(1-\alpha)}$$

$$x = (1-\alpha)^{-1} \quad y = 2(1-\alpha)^{-1} + (1-\alpha) + \gamma\alpha$$

A derivation of the expressions for  $v_i$ ,  $x$ , and  $y$  has been presented by Stern et al. (2).

Carbon dioxide is produced by a secondary process: the water-gas-shift reaction. The stoichiometry of the water-gas-shift reaction is represented by



where  $v'_{H_2O} = v'_{CO} = -1$  and  $v'_{H_2} = v'_{CO_2} = 1$ .

For the synthesis reaction, the rate expression suggested by Dry (3) has been used. Thus,

$$r_{FTS} = \frac{\omega Da_L \theta_{L,CO} \theta_{L,H_2}}{b' \theta_{L,H_2O} + \theta_{L,CO}} \quad (15)$$

where  $Da_L$  is defined

$$Da_L = \frac{k_{FTS} (1-\epsilon_G) \bar{\omega}_L}{U_L m_{H_2}} \quad (16)$$

This rate expression accounts for the inhibition of the synthesis rate by water, an effect which may be important at high conversion. Note that the knowledge of  $U$  or of the water-gas-shift reaction kinetics is required to determine  $\theta_{L,H_2O}$ .

The expression suggested by Moe (4) has been used to determine the rate of the water-gas-shift reaction. Thus,

$$\rho_{WGS} = \omega Da'_L (\theta_{L,H_2O} \theta_{L,CO} - \frac{1}{K} \theta_{L,CO_2} \theta_{L,H_2}) \quad (17)$$

In eq. 19,  $Da'$  is defined

$$Da'_L = \frac{k_{WGS} (1-\epsilon_G) \bar{w}_{LC,G,H_2}}{U_L \bar{m}_{H_2O} \bar{m}_{CO}} \quad (18)$$

The dimensionless rate of production (or consumption) of component  $i$ ,  $\rho_i$ , is given by the sum of the rates of production (or consumption) of that component via the synthesis and water-gas-shift reactions. Thus,

$$\rho_i = v_i \rho_{FTS} + v_i' \rho_{WGS} \quad (19)$$

Equations 3, 6, and 8 constitute a set of second-order, ordinary differential equations. These equations, together with the boundary conditions given by eqns. 4, 5, 7, 9, and 10 were solved by a collocation over a finite element using a subroutine known as COLSYS (5). Equation 11 was solved analytically to obtain  $\omega$  as a function  $\zeta$ . Thus,

$$\omega = \frac{Pe_s \exp(-Pe_s \zeta)}{[1 - \exp(-Pe_s)]} \quad (20)$$

The parameters appearing in the model were evaluated using data and correlations taken from the literature. Specific values of individual parameters can be found in Refs. (3,6).

The model outlined above was solved for a variety of reactor dimensions, gas flow rates, and catalyst activities to establish the extent to which transport parameters ( $k_L a$ ,  $D_L$ ,  $D_G$ , and  $D_S$ ) influence the performance of a bubble column reactor. These calculations together with an analysis of the mass balance equations for the gas and liquid phases led to the conclusion that gas- and liquid-phase dispersion can be neglected when

$$(Da^*)^2 / Pe^* \ll 1 \quad (21)$$

where



$$Pe^* = \frac{[U_L / (U_G^m H_2)] \phi + 1}{[U_L / (U_G^0 m_{H_2})] \phi \epsilon_L / Pe_L + \epsilon_G / Pe_G} \quad (22)$$

$$Da^* = \frac{U_L \phi v_{H_2} Da_L}{U_G^0 (U_L / U_G^0 m_{H_2}) \phi + 1} \quad (23)$$

The condition represented by eqn. 21 is fully satisfied for all laboratory and most pilot-plant scale reactors, but would not be satisfied by reactors used for FTS on an industrial scale.

Inspection of eqn. 20 indicates that  $\omega$  will deviate from unity for  $Pe_s > 1$ . Consequently, axial gradients are to be expected for large catalyst particle diameters and low gas velocities. Where such gradients do occur, it is found that their effects are most severe for values of  $Da_G$  and  $Da_C$  greater than 1.0.

The validity of the proposed model was confirmed by using it to predict the syngas conversion ( $x_{CO+H_2}$ ) and utilization ratio for several laboratory and pilot-plant scale reactors. The effects of  $H_2/CO$  feed ratio and gas velocity on syngas conversion and consumption ratio predicted by the model are in very good agreement with the experimental results reported by Deckwer et al. (7) and Kuo (8). Our analysis suggests that as a result of higher catalyst activity the reactor operated by Deckwer et al. (7) was influenced by gas-liquid mass transfer to a greater extent than that operated by Kuo (8). It also appears that water-gas-shift equilibrium was not fully achieved in the reactor of Deckwer et al. (7) but was in the reactor of Kuo (8). The water-gas-shift reaction causes an increase in the  $H_2/CO$  ratio near the top of the reactor. This effect is most pronounced at high syngas conversions in the presence of a finite resistance to gas-liquid mass transfer. The water-gas-shift equilibrium acts to decrease the stoichiometric coefficient of the limiting reactant, with the result that at high conversion, the syngas consumption ratio approaches the feed  $H_2/CO$  ratio.

Having established that the model accurately describes the performance of small scale reactors, it was used to predict the influence of process and design variables on the performance of large scale reactors. These calculations showed that the most efficient use of a given reactor volume is obtained with small diameter reactors. For a given space time, the conversion goes through a broad maximum as velocity increases. The optimum velocity depends on the variation of  $k_L a$  and  $\epsilon_G$  with velocity, as well as on the catalyst loading and activity. The most effective use of a given mass of catalyst occurs when  $\omega$  is low; however, the highest value of the space-time yield occurs when  $\omega$  is large. Increasing the water-gas-shift activity moves the  $H_2/CO$  utilization ratio closer to the feed  $H_2/CO$  ratio and increases the space-time yield by lowering the rate of  $H_2$  consumption relative to the rate of syngas consumption. Thus, catalysts with high water-gas-shift activity are best suited to processing CO-rich syngas.

### Experimental Studies

The performance of a laboratory-scale bubble-column reactor was investigated using a 5.0% Ru/Al<sub>2</sub>O<sub>3</sub> catalyst. The reactor used for these studies had an ID of 1.8 cm and was 260 cm high. Molten paraffin wax was used to suspend the catalyst.

The product distribution is highly dependent on the partial pressures of H<sub>2</sub> and CO, and on the temperature. For temperatures below about 533 K, strong deviations from a Schulz-Flory distribution are observed in the C<sub>1</sub>-C<sub>3</sub> range. Methane lies above the Schulz-Flory line extrapolated through C<sub>4</sub><sup>+</sup> products, C<sub>2</sub> and C<sub>3</sub> products lie below the line. The deviation of methane from the Schulz-Flory line decreases and the deviation for C<sub>2</sub> and C<sub>3</sub>'s increases with decreasing H<sub>2</sub>/CO ratio of the feed. For temperatures above 533 K, the product distribution closely approximates a Schulz-Flory distribution. The value of  $\alpha$  is a strong function of temperature, decreasing with increasing temperature, but is only weakly dependent on syngas composition.

The kinetics of formation of C<sub>1</sub> to C<sub>4</sub> hydrocarbons are well represented by power-law rate expressions. The parameter values obtained for synthesis in the bubble column reactor are in good agreement with earlier studies with Ru/Al<sub>2</sub>O<sub>3</sub> conducted in fixed-bed reactions. For C<sub>5</sub> and higher products, the rate of product formation can be represented by the rate of forming C<sub>4</sub> products times  $c^{n-4}$ .

The operation of a bubble-column reactor under conditions where gas-liquid mass transfer is significant can be described successfully using a model recently proposed by Stern et al. (3). The model properly predicts the dependence of syngas conversion and H<sub>2</sub>-CO utilization ratio on the feed gas velocity and composition.

During Fischer-Tropsch synthesis, carbon deposits on the catalyst. A part of this deposit is the reactive intermediate involved in hydrocarbon synthesis, while the rest is more refractory carbon which eventually leads to catalyst deactivation. The distribution of carbon forms present on a catalyst can be assessed by isotopic tracer studies. In the course of the present project, a novel mathematical technique was developed for the interpretation of isotopic tracer experiments. The method predicts the distribution of carbon types and the spectrum of carbon reactivities.

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8. Kuo, J. C., DOE Report Contract Number DE-AC22-80PC30022, 1983.

## PUBLICATIONS

The following publications have resulted from work carried out on this project. Copies of these papers are given in the Appendix.

- (1) D. Stern, A. T. Bell, and H. Heinemann, "Effects of Mass Transfer on the Performance of Slurry Reactors Used for Fischer-Tropsch Synthesis", Chem. Eng. Sci. 38, 597 (1983).
- (2) Y. T. Shah, D. Stern, A. T. Bell, and H. Heinemann, "Mass Transfer-Imposed Constraints on Fischer-Tropsch Synthesis in a Slurry Reactor" Proceedings of the International Chemical Reaction and Engineering Meeting, Pune, India, p. 345, 1984.
- (3) D. Stern, A. T. Bell, and H. Heinemann, "A Theoretical Model for the Performance of Bubble-Column Reactors Used for Fischer-Tropsch Synthesis", Chem. Eng. Sci. 40, 1665 (1985).
- (4) D. Stern, A. T. Bell, and H. Heinemann, "Experimental and Theoretical Studies of Fischer-Tropsch Synthesis over Ruthenium in a Bubble-Column Reactor", Chem. Eng. Sci. 40, 1917 (1985).
- (5) D. Stern, A. T. Bell, and H. Heinemann, "Analysis of the Design of Bubble-Column Reactors Used for Fischer-Tropsch Synthesis", I&EC Proc. Design Develop. 24, 1213 (1985).
- (6) M. de Pontes, G. H. Yokomizo, and A. T. Bell, "A Novel Method for Analyzing Transient Responses Data Obtained in Isotopic Tracer Studies of CO Hydrogenation", J. Catal., in press.

*Reprints removed*

## NOTATION

$a$	Interfacial area per unit volume, $\text{cm}^{-1}$ .
$b'$	Dimensionless rate parameter appearing in eqn. 15.
$C_G$	Total gas phase concentration, $\text{mol}/\text{cm}^3$ .
$C_{G,i}$	Gas-phase concentration of component $i$ , $\text{mol}/\text{cm}^3$ .
$C_{G,i}^0$	Inlet gas-phase concentration of component $i$ , $\text{mol}/\text{cm}^3$ .
$C_{L,i}$	Liquid-phase concentration of component $i$ , $\text{mol}/\text{cm}^3$ .
$Da_L, Da_L'$	Dankohler number based on liquid velocity. Defined in eqns. 16, 18.
$D_G$	Gas-phase dispersion coefficient, $\text{cm}^2/\text{s}$ .
$D_i$	Diffusivity for component $i$ , $\text{cm}^2/\text{s}$ .
$D_L$	Liquid-phase dispersion coefficient, $\text{cm}^2/\text{s}$ .
$D_S$	Catalyst dispersion coefficient, $\text{cm}^2/\text{s}$ .
$d$	Reactor diameter, $\text{cm}$ .
$I$	Inlet $\text{H}_2/\text{CO}$ ratio.
$K$	Equilibrium coefficient for the water-gas-shift reaction.
$k_L$	Mass transfer coefficient from gas-liquid interface to bulk liquid, $\text{cm}/\text{s}$ .
$k_{\text{FTS}}$	Rate coefficient for the Fischer-Tropsch synthesis, $\text{cm}^3/\text{g s}$ .
$k_{\text{WGS}}$	Rate coefficient for the water-gas-shift reaction, $(\text{cm}^6/\text{mol})/\text{g s}$ .
$L$	Reactor length, $\text{cm}$ .
$m_i$	Solubility coefficient for component $i$ , $(\text{mol}/\text{cm}^3)_L/(\text{mol}/\text{cm}^3)_G$ .
$n$	Number of carbon atoms in a product molecule.
$N_{G,i}$	Gas-phase Stanton number. Defined in eqn. 2.
$N_{L,i}$	Liquid-phase Stanton number. Defined in eqn. 2.
$Pe_G$	Gas-phase Peclet number. Defined in eqn. 2.
$Pe_L$	Liquid-phase Peclet number. Defined in eqn. 2.

$Pe_S$	Solids Peclet number. Defined in eqn. 2.
$r_i$	Rate of production of component $i$ by the Fischer-Tropsch synthesis reaction, $(\text{mol}/\text{cm}^3)/\text{s}$ .
$r_{\text{FTS}}$	Rate of consumption of $\text{CO}$ and $\text{H}_2$ by the Fischer Tropsch synthesis reaction $(\text{mol}/\text{cm}^3)/\text{s}$ .
$r_{\text{WGS}}$	Rate of the water-gas-shift reaction, $(\text{mol}/\text{cm}^3)/\text{s}$ .
$U$	Utilization ratio, mol $\text{H}_2$ consumed/mol $\text{CO}$ consumed.
$U_G^0$	Inlet gas superficial velocity, $\text{cm}/\text{s}$ .
$U_G$	Gas superficial velocity, $\text{cm}/\text{s}$ .
$U_L$	Liquid superficial velocity, $\text{cm}/\text{s}$ .
$U_S$	Solids settling velocity, $\text{cm}/\text{s}$ .
$w$	Catalyst concentration, $\text{g}/\text{cm}^3$ slurry.
$\bar{w}$	Average catalyst concentration, $\text{g}/\text{cm}^3$ slurry.
$X_i$	Conversion of component $i$ .
$z$	Axial position, $\text{cm}$ .
$\alpha$	Chain growth probability.
$\beta$	Ratio of $\text{H}_2\text{O}$ formation rate to $\text{CO}_2$ formation rate.
$\gamma$	Fraction of products that are paraffins.
$\delta$	Gas contraction factor, $(U_G(X_{\text{H}_2} = 1.0) - U_G^0)/U_G^0$
$\zeta$	Dimensionless axial position.
$\theta_G$	Dimensionless total gas concentration.
$\theta_{G,i}$	Dimensionless gas phase concentration of component $i$ .
$\theta_{G,i}^0$	Dimensionless inlet gas phase concentration of component $i$ .
$\theta_{L,i}$	Dimensionless liquid phase concentration of component $i$ .
$\theta_{L,i}^0$	Dimensionless inlet liquid phase concentration of component $i$ .
$\rho_i$	Dimensionless rate of production of component $i$ . Defined in eqn. 19.

- $\rho_{\text{FTS}}$  Dimensionless rate of consumption of CO and H<sub>2</sub> by the synthesis reaction.
- $\rho_{\text{WGS}}$  Dimensionless rate of the water-gas-shift reaction.
- $v_i$  Stoichiometric coefficient for consumption of component i by the Fischer-Tropsch synthesis reaction.
- $v_i'$  Stoichiometric coefficient for consumption of component i by the water-gas-shift reaction.
- $v_i^-$  Stoichiometric coefficient for component i when  $v_i$  do not depend on concentrations of H<sub>2</sub>, CO, CO<sub>2</sub>, or H<sub>2</sub>O.
- $u$  Dimensionless gas velocity.
- $\omega$  Dimensionless catalyst concentration.

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