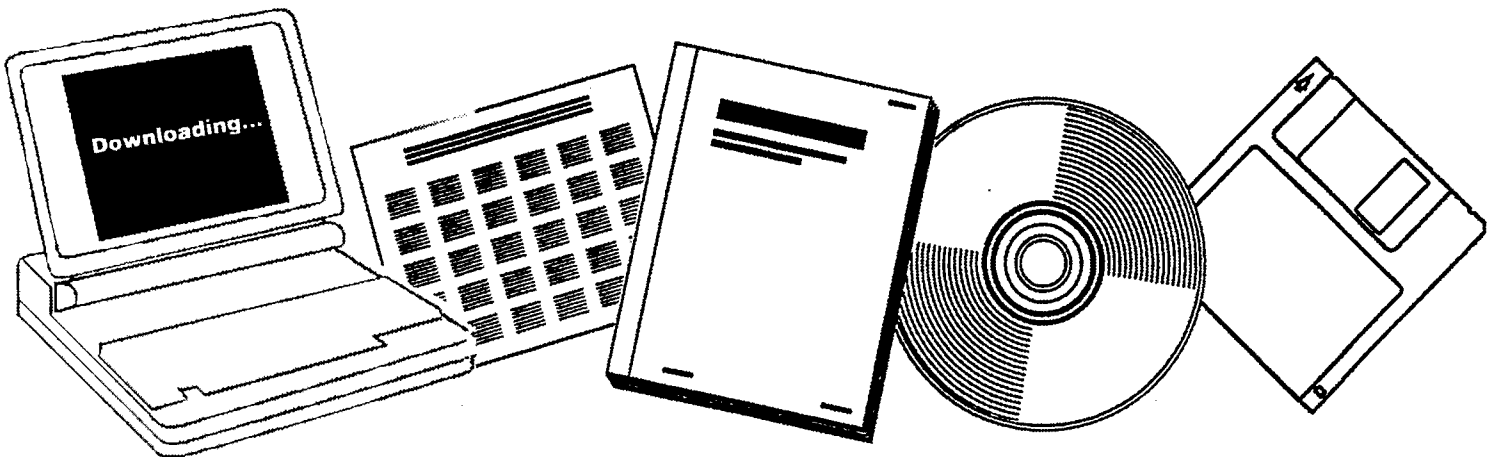# CONVERSION OF LOW H SUB 2 /CO RATIO SYNTHESIS GAS TO HYDROCARBONS: FINAL REPORT, OCTOBER 1, 1981-SEPTEMBER 30, 1986

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Final Report

Conversion of Low H_2/CO Ratio
Synthesis Gas to Hydrocarbons

DOE Project DE-FG22-81PC40795

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DISCLAIMER

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

$$Pe_s = \frac{(U_s - U_L/\varepsilon_L)L}{D_s} \quad .$$

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 comonent i is written:

$$\frac{\varepsilon_G}{Pe_G} \frac{d^2 \theta_{G,i}}{d\zeta^2} - \frac{d(\upsilon \theta_{G,i})}{d\zeta} - N_{G,i}(\theta_{G,i} - \theta_{L,i}) = 0. \tag{3}$$

The boundary conditions on eq. (3) are:

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

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

To determine υ, 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,

$$\theta_G \frac{d\upsilon}{d\zeta} \sum_i N_{G,i}(\theta_{G,i} - \theta_{L,i}) = 0. \tag{6}$$

The boundary condition on eq. (6) is:

$$\upsilon = 1 \quad \text{at} \quad \zeta = 0. \tag{7}$$

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

3.

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

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

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

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

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 esentially constant along the column length, the mass balance on catalyst can be written:

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

The boundary conditions on eq. 11 are:

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

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

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

$$1 \qquad |\nu_{CO}|CO + |\nu_{H_2}|H_2 \rightarrow |\nu_{HC}|C_xH_y + |\nu_{H_2O}|H_2O$$
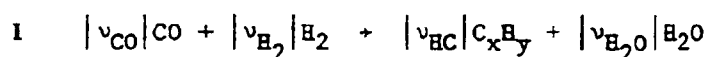
The values of ν_i, x, and y depend on the probability of chain growth, α, and the overall fraction of C_2^+ paraffins, γ. Thus,

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

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

(14)

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

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

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

A derivation of the expressions for ν_i, x, and y has been presensted 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

$$2 \qquad |\nu'_{H_2O}|H_2O + |\nu'_{CO}|CO \; \rightleftarrows \; |\nu'_{CO_2}|CO_2 + |\nu'_{H_2}|H_2$$
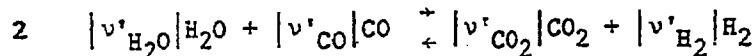
where $\nu'_{H_2O} = \nu'_{CO} = -1$ and $\nu'_{H_2} = \nu'_{CO_2} = 1$.

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

$$\rho_{FTS} = \frac{\omega Da_L \theta_{L,CO} \theta_{L,H_2}}{b' \theta_{L,H_2O} + \theta_{L,CO}}$$

(15)

where Da_L is defined

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

(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 θ_{L,H_2O}.

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

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

In eq. 19, Da' is defined

$$Da'_L = \frac{k_{WGS}(1-\varepsilon_G)\bar{\omega}LC_{G,H_2}}{U_L{}^m_{H_2O}{}^m_{CO}} \tag{18}$$

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

$$\rho_i = \nu_i \rho_{FTS} + \nu'_i\,\rho_{WGS} \tag{19}$$

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 obtaine ω as a function ζ. Thus,

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

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 ooutlined above was solved for a variety of reactor dimensions, gas flow rates, and catalyst activities to establish the extent to which transport parameters (k_La, 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

$$(Da^*)^2/Pe^* \ll 1 \tag{21}$$

where

$$Pe^* = \frac{[U_L/(U_G m_{H_2})]\phi + 1}{[U_L/(U_G^0 m_{H_2})]\phi\varepsilon_L/Pe_L + \varepsilon_G/Pe_G]} \qquad (22)$$

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

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 ω will deviate from unity for $Fe_s > 1$. 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_G 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 ε_G with velocity, as well as on the catalyst loading and activity. The most effective use of a given mass of catalyst occurs when ω is low; however, the highest value of the space-time yield occurs when ω 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_2O_3 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 product distribution is highly dependent on the partial pressures of H_2 and CO, and on the temperature. For temperatures below about 533 K, strong deviations from a Schulz-Flory distribution are observed in the C_1-C_3 range. Methane lies above the Schulz-Flory line extrapolated through C_4^+ products, C_2 and C_3 products lie below the line. The deviation of methane form the Schulz-Flory line decreases and the deviation for C_2 and C_3's increases with decreasing H_2/CO ratio of the feed. For temperatures above 533 K, the product distribution closely approximates a Schulz-Flory distribution. The value of α is a strong function of temperature, decreasing with increasing temperature, but is only weakly dependent on syngas composition.

The kinetics of formation of C_1 to C_4 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_2O_3 conducted in fixed-bed reactions. For C_5 and higher products, the rate of product formation can be represented by the rate of forming C_4 products times c^{n-4}.

The operation of a bubble-column reactor under conditions where gas-liquid mass transfer is significant can be desceribed successfully using a model recently proposed by Stern et al. (3). The model properly predicts the dependence of syngas conversion and H_2-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 with 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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4. Moe, J., Chem. Eng. Prog. 58, 33 (1962).
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7. Deckwer, W.-D., Serpemen, Y., Ralek, M., and Schmidt, B., I&EC Proc. Des. Dev. 21, 222 (1982).
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 sa 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, cm^{-1}.
b'	Dimensionless rate parameter appearing in eqn. 15.
C_G	Total gas phase concentration, mol/cm^3.
$C_{G,i}$	Gas-phase concentration of component i, mol/cm^3.
$C_{G,i}^o$	Inlet gas-phase concentration of component i, mol/cm^3
$C_{L,i}$	Liquid-phase concentration of component i, mol/cm^3.
Da_L, Da_L'	Damkohler number based on liquid velocity. Defined in eqns. 16, 18.
D_G	Gas-phase dispersion coefficient, cm^2/s.
D_i	Diffusivity for component i, cm^2/s.
D_L	Liquid-phase dispersion coefficient, cm^2/s.
D_S	Catalyst dispersion coefficient, cm^2/s.
d	Reactor diameter, cm.
I	Inlet H_2/CO ratio.
K	Equilibrium coefficient for the water-gas-shift reaction.
k_L	Mass transfer coefficient from gas-liquid interface to bulk liquid, cm/s.
k_{FTS}	Rate coefficient for the Fischer-Tropsch synthesis, cm^3/g s.
k_{WGS}	Rate coefficient for the water-gas-shift reaction, $(cm^6/mol)/g$ s.
L	Reactor length, cm.
m_i	Solubility coefficient for component i, $(mol/cm^3)_L/(mol/cm^3)_G$.
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, $(mol/cm^3)/s$.

r_{FTS} Rate of consumption of CO and H_2 by the Fischer Tropsch synthesis reaction $(mol/cm^3)/s$.

r_{WGS} Rate of the water-gas-shift reaction, $(mol/cm^3)/s$.

U   Utilization ratio, mol H_2 consumed/mol CO consumed.

U_G^0 :   Inlet gas superficial velocity, cm/s.

U_G Gas superficial velocity, cm/s.

U_L Liquid superficial velocity, cm/s.

U_S Solids settling velocity, cm/s.

w   Catalyst concentration, g/cm^3 slurry.

$\bar{w}$ Average catalyst concentration, g/cm^3 slurry.

X_i Conversion of component i.

z   Axial position, cm.

α Chain growth probability.

β Ratio of H_2O formation rate to CO_2 formation rate.

γ Fraction of products that are paraffins.

δ Gas contraction factor, $(U_G(X_{H_2}= 1.0) - U_G^0)/U_G^0)$

ζ Dimensionless axial position.

θ_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.

ρ_i Dimensionless rate of production of component i. Defined in eqn. 19.

ρ_{FTS} Dimensionless rate of consumption of CO and H_2 by the synthesis reaction.

ρ_{WGS} Dimensionless rate of the water-gas-shift reaction.

ν_i Stoichiometric coefficient for consumption of component i by the Fischer-Tropsch synthesis reaction.

ν_i' Stoichiometric coefficient for consumption of component i by the water-gas-shift reaction.

$\bar{\nu}_i$ Stoichiometric coefficient for component i when ν_i do not depend on concentrations of H_2, CO, CO_2, or H_2O.

υ Dimensionless gas velocity.

ω Dimensionless catalyst concentration.

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