

APPENDIX A

SLURRY REACTOR DESIGN STUDIES

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Effect of H/CO Ratio on Fischer-Tropsch Synthesis Reaction (Slurry vs Fixed-Bed) "The Boudouard Reaction"

The Boudouard Reaction is the carbon formation from CO, and is given by:



This carbon formation is associated with catalyst particle swelling and formation of graphite nuclei within the catalyst crystallites that create stresses which disintegrate the particle which eventually leads to bed plugging, maldistribution of the feed, and hot spots. In Fischer-Tropsch synthesis on fixed-bed, gas phase reactors, as the H/CO ratio⁸ goes down and the temperature increases, the selectivity to the Boudouard reaction increases. For this reason, fixed bed Fischer-Tropsch synthesis reactor is run at sufficiently low temperatures and with high H/CO ratios, SASOL reportedly uses H/CO ratios of about 6 [Dry 1980; Dry et. al. (1976); Stern et. al. (1983)].

Dry has correlated the rate of coke formation with $(P_{\text{CO}}/P_{\text{H}}^3)$ (Dry et al., 1976) and with $(P_{\text{CO}}/P_{\text{H}}^2)$ (Dry, 1980) where P_i are the partial pressures. So the rate of coke formation, r_c is given by:

$$r_c = k \cdot (P_{\text{CO}}/P_{\text{H}}^3) \quad \text{or} \quad k' \cdot (P_{\text{CO}}/P_{\text{H}}^2)$$

Thus when the H/CO ratio decreases from 2 to 1, the coke formation rate increases from $0.25 k'$ to k' . Dry (1980) shows the temperature dependency of k' , at a temperature T_1 , $k' = 1.0$ and at T_2 , $k' = 2.0$. The temperatures are not specified in that study.

For a fixed bed reactor operating in the gas phase, the rate of coke formation should be applied integrally over the whole length of catalyst bed to derive the overall carbon deposition rate. As conversion by the F-T reaction increases down the reactor, H/CO ratio decreases resulting in higher rates of coke formation as we go down the reactor. However, higher temperatures are experienced at the inlet which also increases the rate of coke

⁸ In this writeup, H₂ is abbreviated as H.

formation. Dry (1980) indicates that the rate of coke formation is approximately constant over the whole bed. However, he studied H/CO ratios of 4-6, which are much higher than the desired ratio of 0.7-1.

When the process is carried in a slurry reactor, the effective H/CO ratio the catalyst sees is the concentration in the liquid phase which is controlled by the vapor-liquid equilibrium and the mass transfer rates.

If the reaction is kinetics-controlled, i.e., the reaction rate is slow enough so that the concentration in the liquid phase is uniform, then the effective H/CO ratio the catalyst particle sees is the ratio of solubilities of hydrogen and CO in the liquid phase. If we assume Henry's Law,

$$P_i = H_i \cdot C_i$$

then the solubility ratio C_H/C_{CO} is given by,

$$C_H/C_{CO} = (P_H/H_H) \cdot (H_{CO}/P_{CO}) = (P_H/P_{CO}) \cdot (H_{CO}/H_H)$$

The data on the Henry's Law constants are somewhat scattered:

Stern et al. (1983) give $H_{CO}/H_H = 0.75$ based on Peter and Weinert's classic work (Peter & Weinert 1955).

Air Products Report gives $H_{CO} = 0.91$ for methanol synthesis in liquid Freezene-100.

Matsumoto and Satterfield (1984) report:

$$\begin{aligned} H_{CO}/H_H &= 0.91 \text{ for octacosane at } 250^\circ\text{C} \\ &= 1.08 \text{ for phenanthrene at } 250^\circ\text{C} \end{aligned}$$

Deckwer, et.al. give $H_{CO}/H_H = 1.60$ at 250°C

Based on these values, for $P_H/P_{CO} = 0.7$,

$$C_H/C_{CO} = 0.5 - 1.12$$

Therefore, if we have reaction control, the effective H/CO concentration the particle sees would not be much different from a gas phase reaction.

At the other extreme, if the reaction is mass transfer controlled, then the mass flux would be:

$$J_i = -D_i \cdot (dC_i / dx) = -D_i \cdot (\Delta C_i / \delta) = D_i \cdot C_i$$

What the catalyst sees would be the flux ratio, J_H/J_{CO}

$$\therefore J_H/J_{CO} = (D_H/D_{CO}) \cdot (C_H/C_{CO}) = (D_H/D_{CO}) \cdot (H_{CO}/H_H) \cdot (P_H/P_{CO})$$

We have measured the diffusion coefficient of hydrogen and CO in octacosane, and in F-T wax. D_H/D_{CO} is about 3.0 at F-T conditions. Hence, for $P_H/P_{CO} = 0.7$ the flux ratio (Akgerman 1988):

$$J_H/J_{CO} = 1.5 - 3.36$$

depending on the values of the Henry's Law Constants. Thus the catalyst sees a higher concentration ratio than the gas phase.

If the process is gas-liquid mass transfer controlled, then the H/CO ratio the catalyst sees would be the ratio of mass transfer coefficients:

$(k_{La} H)/(k_{La} CO)$	\propto	$D^{0.376}$	Hughmark, 1962
	\propto	$D^{0.6}$	Akita & Yoshida, 1973
	\propto	$D^{0.667}$	Calderbank & Moo Young, 1961

where D is the ratio D_H/D_{CO} .

Using a value of $D_H/D_{CO} = 3.0$,

$$(k_{La} H)/(k_{La} CO) = 1.5 - 2.0$$

depending on the mass transfer coefficient calculation.

Thus, for mass transfer control, the H/CO ratio the catalyst particle sees is significantly higher than the ratio in the gas phase.

The above analysis is valid for Fischer-Tropsch or methanol synthesis. However, the Boudouard reaction is active on an iron catalyst with iron carbide sites. Therefore, it is important for the F-T reaction only. There is no reference to the Boudouard reaction on methanol synthesis catalyst. The choice of slurry reactor there is based on superior heat transfer characteristics and higher conversion per pass due to shift of kinetic equilibrium.

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DESIGN OF SLURRY REACTORS

A. Suspension of the Solids

Reference: Roy, N. K., D. K. Guha, M. N. Rao. "Suspension of Solids in a Bubbling Liquid; Critical Gas Flow Rates for Complete Suspension", Chem. Eng. Sci., 19, 215 (1964).

Roy et al. derived a correlation, using dimensional analysis, for critical solid hold up, i.e. the maximum amount that can be kept in complete suspension for a given slurry reactor.

$$H_s = 6.84 \times 10^{-4} C_\mu N_{Re} N_B^{-0.23} \left(\frac{u_t}{u_B} \right)^{-0.18} \left(\frac{1}{\tau^1} \right)^{-3.0}$$

for $R_e < 500$

$$H_s = 1.072 \times 10^{-1} C_\mu N_{Re}^{0.2} N_B^{-0.23} \left(\frac{u_t}{u_B} \right)^{-0.18} \left(\frac{1}{\tau^1} \right)^{-3.0}$$

for $R_e > 600$

H_s - Critical Solids hold-up (weight portion of solids)

$C_\mu = 1 - 5.892 \times 10^{-1} \log \mu_L + 1.026 \times 10^{-1} (\log \mu_L)^2$ where μ_L is the liquid viscosity in cP.

N_{Re} - gas phase Reynolds number based on superficial velocity $\frac{d_T \rho_g u_g}{\mu_g}$

d_T - column diameter

ρ_g - gas density

u_g - gas superficial velocity based on empty cross section area

μ_g - gas viscosity

$N_B = \frac{\sigma_L \epsilon_g}{u_g \mu_L}$

σ_L - surface tension of liquid

ϵ_g - gas holdup

u_B - bubble velocity, u_g/ϵ_g

u_t - Stoke's free settling velocity = $\frac{g d_p^2 (\rho_s - \rho_L)}{18 \mu_L}$

d_p - particle diameter

ρ_s - solid density

ρ_L - liquid density

γ^1 - wettability factor, taken unity for most catalysts.

I have used

u_g - 0.41 - 0.5 ft/s

$\gamma' = 1.0$

μ_L - 2 cp

$\rho_g = 7 \times 10^{-3} \text{ g/cm}^3$

σ_L - 16.5 dynes/cm

$\rho_s = 1.7$

$\rho_L = 0.8$

and the dimension of the La Porte reactor, this gives a solids loading (max) of 65%. So up to 45% solids should be easy to suspend.

B. Design Model

Both the F-T synthesis and the MeOH synthesis in slurry reactor involve gas phase reactants dissolving in the liquid, diffusing to the catalyst particle and reaction on the catalyst surface. Since the catalyst particles are small, $\sim 50\mu$, internal diffusion effects would probably be negligible; an effectiveness factor of unity. However, this assumption can be relaxed if needed.

The Thiele modulus for a 1st order reaction is

$$\theta = L \sqrt{\frac{k}{D_{\text{eff}}}}$$

Deckwer et al. (Chem. Eng. Sci., 36, 765 (1981)) give an overall first order rate constant of $0.02 - 0.4 \text{ s}^{-1}$ (based on synthesis gas consumption) for Fischer-Tropsch. The constant is $0.01 - 0.2 \text{ s}^{-1}$ for hydrogen consumption. $D_{\text{H}_2\text{-slurry}} = 54 \times 10^{-5} \text{ cm}^2/\text{s}$ $L = 50 \text{ } \mu\text{m}/6 = 50 \times 10^{-4} \text{ cm}/6$ for spherical particles

$$\therefore \theta = \frac{50 \times 10^{-4}}{6} \sqrt{\frac{0.2}{54 \times 10^{-5}}} = 0.016$$

which corresponds to an effectiveness factor of unity. For $k = 0.01 \text{ s}^{-1}$, $\theta = 0.004$; thus the internal diffusion effects are probably negligible. For methanol synthesis, there is no simple 1st order pseudo rate expression. However, one can use the Weisz Modulus

$$\Phi = \phi^2 \eta = \frac{R \cdot L^2}{C_s \cdot D_{\text{eff}}}$$

Where R is the rate, C_s is the surface concentration. If $\Phi < 0.015$, pore diffusion effects are negligible. There is a rate expression given by v. Wedel et al. von Wedel, W., S. Ledakowicz, W. D. Deckwer, Chem. Eng. Sci. 43, 2169 (1988). Which correlates data from 7 sources.

$$R = 1.98 \times 10^7 \exp(-56343/RT) P_{\text{H}_2}^{0.4} P_{\text{CO}}^{0.18} - 2.15 \times 10^{10}$$

$$\exp(-85930/RT) P_{\text{MeOH}}^{0.13}$$

if we take the maximum value of the rate, at the reactor entrance, then the second term can be neglected. At a total pressure of 1000 psia (6.895 MPa), 250C (523K) and H/CO ratio of 0.7,

Rate = 91.18 kmol/kg h

Using $L = R/3$, 25 $\mu\text{m}/3$

$$C_s = \text{Hydrogen solubility at these conditions} = \frac{100 \text{ kmol}}{\text{m}^3}$$

$$D_{\text{eff}} = 50 \times 10^{-5} \text{ cm}^2/\text{s}$$

$$\text{gives } \phi = 7 \times 10^{-4}$$

If we use the rate expression given by Air Products, $R = 89.55 \text{ mol/kg h}$ which will give a similar ϕ . (Note: I have interpreted the "mol" in rate expression as "kmol", if they are taken as "g mol" then ϕ is even smaller). So for all practical purposes, we can safely assume that the internal diffusion effects are negligible for 50 μm particles both for the Fischer Tropsch and the methanol synthesis reaction.

C. Design Equations - Parametric Analysis

References:

Chaudhari, R. V., P. A. Ramachandran, AIChEJ, 26, 177 (1980).

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Deckwer, W. D., Y. Serpemen, M. Ralek, B. Schmidt, Ind. & Eng. Chem. Process Des. Dev., 21, 231 (1982).

Deckwer, W. D., in "Chemical Reactor Design and Technology", H. I. de Lasa, Editor, Martinus Nijhoff Pub., NATO ASI Series E - No. 110, pp. 411-461, 1986.

In the following analysis, I have first developed a simple model to estimate the effects of various parameters, which is then extended to a more realistic model.

The simple model assumes plug flow in the gas phase and perfectly mixed liquid phase. This would be a realistic model at high gas velocities and at low column height/diameter ratios. Our analysis is based on material balance equations for a single component, although they have to be written for each reactant.

Gas phase:

$$-u_g \frac{dP_A}{dz} = k_g a (P_A - P_{A1})$$

u_g : gas velocity

P_A : partial pressure

P_{A1} : interface concentration

$k_g a$: gas side mass transfer coeff. x area.

But by Henry's Law $P_{A1} = H_A C_{A1}$ and through steady state assumption

$$k_g a (P_A - P_{A1}) = k_L a (C_{A1} - C_A)$$

where $k_L a$ is the liquid side resistance, C_A is the liquid concentration and C_{A1} interface concentration at the liquid side.

If the equations are solved eliminating C_{A1} and P_{A1}

$$-u_g \frac{dP_A}{dz} = \frac{1}{\frac{1}{H_A k_{gA}} + \frac{1}{k_{LA}}} \left[\frac{P_A}{H_A} - C_A \right] = (K_L)_A \left[\frac{P_A}{H_A} - C_A \right]$$

where $(K_L)_A$ is the overall resistance,

If we assume that the liquid phase is perfectly mixed, then $C_A \neq f(z)$ and the above equation can be integrated with the inlet condition at $z = 0$ $P_A = P_A^0$ yielding

$$\frac{P_A - H_A C_A}{P_A^0 - H_A C_A} = \exp(-\alpha_A z) \text{ where } \alpha_A = \frac{(K_L a) A}{u_g H_A}$$

The partial pressure at the column exit, at $z = L$ is P_A^I .

$$\therefore P_A^I = P_A^0 \exp(-\alpha_A L) + H_{AA} C_A (1 - \exp(-\alpha_A L))$$

The average rate of absorption is then given by

$$R_A = \frac{P_A^0 - P_A^f}{\bar{t}} \quad \text{where } \bar{t} \text{ is the residence time}$$

$$\text{and } \bar{t} = \frac{V}{Q_g} \quad \begin{array}{l} Q_g : \text{gas flow rate} \\ V_g : \text{total slurry volume} \end{array}$$

$$\therefore R_A = \frac{Q_H A}{V} \left[1 - \exp(-\alpha_A L) \right] \left[\frac{P_A^0}{H_A} - C_A \right]$$

This absorption rate is the mass transfer rate from the bulk of the gas to the bulk of the liquid. This rate should equal to the rate of mass transfer to the surface of the catalyst particle.

$$\therefore R_A = (k_s a)_A (C_A - C_{AS})$$

$$= \frac{Q H_A}{V} (1 - \exp(-\alpha_A L)) \left[\frac{P_A^0}{H_A} - C_A \right]$$

Eliminating C_A between these equations yields

$$R_A = \frac{1}{\frac{Q H_A}{V} (1 - \exp(-\alpha_A L)) + \frac{1}{(k_s a)_A}} \left[\frac{P_A^0}{H_A} - C_{AS} \right]$$

Now the total driving force is the difference between the inlet concentration and the surface concentration.

We can write $R_A = (M.T.R)_A \left[\frac{P_A^0}{H_A} - C_{AS} \right]$

where the mass transfer resistance for A is given by

$$(M.T.R)_A = \left[\frac{1}{\frac{Q H_A}{V} (1 - \exp(-\alpha_A L))} + \frac{1}{(k_s a)_A} \right]^{-1}$$

If we examine this equation

a. If gases are sparingly soluble $H_A \gg 1.0$

$$\therefore \frac{1}{H_A k_s a} \ll \frac{1}{k_L a}$$

and then $(K_L a)_A = (k_L a)_A$ and $\alpha_A \ll 1$

then $\exp(-\alpha_A L) = 1 - \alpha_A L$

and

$$\frac{Q_g H_A}{V} (1 - \exp(-\alpha_A L)) = \frac{Q_g H_A \alpha_A L}{V} = \frac{Q_g H_A}{V} \cdot \frac{k_L a}{u_g H_A} \cdot L$$

$$u_g = Q_g / \text{Area} \quad V = \text{Area} \times L$$

$$\therefore \frac{Q_g H_A}{V} (1 - \exp(-\alpha_A L)) = k_L a$$

$$\text{and } (M.T.R)_A = \left[\frac{1}{(k_L a)_A} + \frac{1}{(k_{sp})_A} \right]^{-1}$$

This indicates that varying the gas phase concentration will not affect the M.T.R

b. If the gases are highly soluble

$$H_A \ll 1.0$$

$$\therefore \exp(-\alpha_A L) \rightarrow 0$$

$$\text{and } \frac{H_A Q_g}{V} (1 - \exp(-\alpha_A L)) = \frac{Q_g H_A}{V}$$

$$\text{and } (M.T.R)_A = \left[\frac{V}{Q_g H_A} + \frac{1}{(k_{sp})_A} \right]^{-1}$$

$$= (k_{sp})_A \text{ for most cases}$$

Indicating gas to liquid resistance has no significance. If there is a component B, the second reactant, we have similar equations

$$R_B = \nu R_A = (M.T.R)_B \left[\frac{P_B^0}{H_B} - C_{Bs} \right]$$

with

$$(M.T.R)_B = \left[\frac{1}{\frac{H_B Q}{V} (1 - \exp(-\alpha_B L))} + \frac{1}{(k_{s,p})_B} \right]^{-1}$$

First Order Reaction

$$r_A = k_r C_{AS} \cdot W$$

k_r = rate constant in t^{-1}
 W = catalyst mass/unit volume
 r_A = rxn rate.

Since $R_A = r_A$

$$(M.T.R)_A \left(\frac{P_A^0}{H_A} - C_{AS} \right) = W k_r C_{AS}$$

eliminate C_{AS}

$$R_A = r_A = \frac{P_A^0}{H_A} \left[\frac{1}{(M.T.R)_A} + \frac{1}{W k_r} \right]^{-1} = K \frac{P_A^0}{H_A}$$

where K is the overall rate constant

$$K = \left[\frac{1}{\frac{H_A Q}{V} (1 - \exp(-\alpha_A L))} + \frac{1}{(k_{s,p})_A} + \frac{1}{W k_r} \right]^{-1}$$

Let's analyze K

For Fischer-Tropsch and Methanol Synthesis reaction the literature indicates that the

$$\frac{H_A Q}{V} (1 - \exp(-\alpha_A L)) = (k_{L,a})_A$$

$$\therefore K = \left[\frac{1}{k_{L,a}} + \frac{1}{k_{s,p}} + \frac{1}{W k_r} \right]^{-1}$$

where k_T is a pseudo first order rate constant.

For Fischer-Tropsch and MeOH synthesis the physicochemical properties of the liquid phase is about the same.

$k_L a$: Although there are many correlations, all the data in the literature indicate that $k_L a = 0.1 - 0.2 \text{ s}^{-1}$ the maximum value reported being $k_L a = 0.4 \text{ s}^{-1}$.

$k_{s,p}$: We use the correlation by Sanger & Deckwer (Sanger, P., W. D. Deckwer, Chem. Eng. J., 22, 179 (1981)).

$$Sh = 2.0 + 0.545 Sc^{1/3} \left[\frac{\epsilon d_p^4}{\nu^3} \right]^{0.264} \quad Sh: \frac{k_{s,p} d_p}{D}$$

$$\text{with } \epsilon = u_g \cdot g$$

$$Sc: \frac{\nu}{D}$$

Using $D = 50 \times 10^{-5} \text{ cm}^2/\text{s}$ for H_2 , $20 \times 10^{-5} \text{ cm}^2/\text{s}$ for CO

$$\mu = 2 \text{ cp}$$

$$\rho_L = 0.8 \text{ g/cm}^3$$

$$d_p = 50 \text{ }\mu\text{m}$$

$$u = 0.5 \text{ ft/s} = 15 \text{ cm/s}$$

$$g = 980 \text{ cm/s}^2$$

$$(Sh)_{\text{H}_2} = 3.74$$

$$k_s = 0.374 \text{ cm/s}$$

$$(Sh)_{\text{CO}} = 4.37$$

$$k_s = 0.175 \text{ cm/s}$$

The liquid-solid interphase area a_p is

$$a_p = \frac{6 \epsilon_p}{d_p}$$

For 35% loading, 50 μ m particles $a_p = 420 \text{ cm}^{-1}$

$$\therefore k_s a_p = 157 \text{ for } H_2 \\ 74 \text{ for } CO.$$

wk_r : The reported values of wk_r vary in the literature. For Fischer Tropsch Reaction, it is in the range $0.02 - 0.4 \text{ s}^{-1}$ as mentioned on p. 3 of this report

$$K = \left[\frac{1}{0.1 - 0.2} + \frac{1}{74 - 157} + \frac{1}{0.02 - 0.4} \right]^{-1}$$

Obviously, $k_s a_p \gg k_L a$ and wk_r and hence the liquid solid mass transfer resistance can be neglected in analysis. $k_L a$ is a strong function of solids suspension, solid loading, gas holdup, etc., and its value may decrease by an order of magnitude making it the controlling resistance. However, the reactor design should include both the gas-liquid mass transfer and the reaction rate terms. Liquid-solid mass transfer and diffusion into solid particle may be neglected based on the analysis presented in previous pages. Relative magnitude of these resistances will not change if a more complicated rate and hydrodynamic model is employed.

D. Design Equations - Model Development

Assumption

1. Plug flow in the gas phase - justified in terms of the high gas velocities.
2. Axial Dispersion in the liquid phase

3. Isothermal
4. Non-uniform catalyst distribution → use of sedimentation dispersion model.
5. Constant pressure → implies the influence of hydrostatic head on gas expansion and fluid properties is negligible.
6. Change in gas flow rate due to gas consumption and change in number of moles.
7. Change in gas holdup along the reactor.

A. GAS PHASE

$$-\frac{d}{dz} (u_g P_A) - (k_L a)_A \left[\frac{P_A}{H_A} - C_A \right] = 0$$

$$-\frac{d}{dz} (u_g P_B) - (k_L a)_B \left[\frac{P_B}{H_B} - C_B \right] = 0$$

B. LIQUID PHASE

$$\epsilon_L D_L \frac{d^2 C_A}{dz^2} + (k_L a)_A \left(\frac{P_A}{H_A} - C_A \right) - \underbrace{u_L \frac{dC_A}{dz}}_{\substack{\text{is 0 if liquid} \\ \text{batch}}} - \underbrace{\epsilon_L R_A}_{\substack{\text{rxn rate} \\ \text{term}}} = 0$$

$$\epsilon_L D_L \frac{d^2 C_B}{dz^2} + (k_L a)_B \left[\frac{P_B}{H_B} - C_B \right] - \underbrace{u_L \frac{dC_B}{dz}}_{\substack{\text{coefficient}}} - \underbrace{\epsilon_L \nu R_A}_{\substack{\text{stoichiometric}}} = 0$$

The variable gas velocity is given by

$$u_G = u_{G0} (1 + \alpha x_{A+B})$$

$$\alpha \text{ is the contraction factor} = \frac{Q_g \text{ at } x_{A+B} - 1 - Q_g \text{ at } x_{A+B} = 0}{Q_g \text{ at } x_{A+B} = 0}$$

x_{A+B} is the total synthesis gas conversion x_{H+CO}

Q_g - volumetric flow rate of gas

u_{Go} - inlet superficial gas velocity

x_{A+B} is related to x_A or x_B , conversion of A or B, through the usage ratio and inlet molar ratio.

$$x_{A+B} = \frac{1+U_B}{1+I_B} x_A = \frac{1+U_A}{1+I_A} x_B$$

$$U_B = \text{usage ratio} = \frac{\text{change in \# of moles of B}}{\text{change in \# of moles of A}}, \quad U_A = \frac{1}{U_B}$$

I_B - inlet B/A molar ratio (I_A - A/B ratio)

$$x_A = \text{conversion of A} = \frac{u_{Go} y_{Ao} - u_G y_A}{u_{Go} y_{Ao}}$$

y_{Ao} and y_A are A mole fraction at the inlet and at z , in the gas phase

$$x_A = 1 - \frac{u_G y_A}{u_{Go} y_{Ao}} = 1 - \bar{u}_G \bar{y}_A$$

where \bar{u}_G and \bar{y}_A are dimensionless gas velocity and mole fraction

These equations can be put in dimensionless form for dimensionless profiles

(See Deckwer et al., Ind. & Eng. Chem., Process Des. Dev. 21, 231 (1982).)

E. Solids Dispersion

An important phenomenon in bubble column slurry reactors is the suspension and axial dispersion of solids. For bubble column slurry

operation two suspension states may exist; namely complete suspension in which all particles are in suspension and homogeneous suspension in which particle concentration is uniform throughout the reactor. We have already presented the criteria of Roy et al. (1964) for determining the maximum amount of solids that can be kept in complete suspension for a given operating condition and have shown that for Fischer-Tropsch and Methanol Synthesis reactors, theoretically up to 60% can be suspended.

In bubble column slurry reactors there is a solids distribution with height.

Reference: Kato, Y., A. Nishiwaki, T. Fukuda, S. Touka, J. Chem. Eng. Japan, 5, 112 (1972).

The solids distribution effect is more significant in columns with large L/d_t ratios. The effect of this profile on reaction rate is obvious, if the catalyst particles are not well dispersed, the reactor space time yields will suffer.

Normally, for catalytic reactors, the reaction rate is expressed in terms of

$$R = \frac{\text{moles product}}{\text{unit weight catalyst} \times \text{time}}$$

If there is uniform catalyst loading, this quantity R multiplied by the total density of the catalyst in weight/volume, yields the reactor size for a specified conversion. If the catalyst dispersion is not uniform; i.e., there is a catalyst concentration profile in the reactor; then, in the model equations, instead of R, one must use $R \cdot C_{cat}$ where C_{cat} is the catalyst concentration in weight/volume, and

integrate the equation over the reactor length. For slurry bubble columns this concentration can be calculated from the dispersion/sedimentation model. For batch suspension, this model yields

$$D_c \frac{d^2 C_{cat}}{dz^2} + u_{cs} \frac{dC_{cat}}{dz} = 0$$

D_c = dispersion coefficient for the catalyst particles

u_{cs} = settling velocity of catalyst particles

For Batch Slurry: The solution of this equation, with the appropriate boundary conditions yields

$$C_{cat}(z) = (C_{cat})_{avg} \frac{\frac{u_{cs} L}{D_c} \exp\left(-\frac{u_{cs} z}{D_c}\right)}{1 - \exp\left(-\frac{u_{cs} L}{D_c}\right)}$$

where $(C_{cat})_{avg}$ is the mean catalyst concentration.

If the liquid is also flowing, the equation then becomes

$$D_c \frac{d^2 C_{cat}}{dz^2} + \left[u_{cs} - \frac{u_L}{1 - \epsilon_g} \right] \frac{dC_{cat}}{dz} = 0$$

(Reference: Ozturk, S. S., Y. T. Shah, W. D. Deckwer, Chem. Eng. J., 37, 177 (1988)).

the solution then becomes

$$C_{cat} = (C_{cat})_{feed} \frac{\exp\left[\left(\frac{u_{cs} L}{D_c} - \frac{u_L L}{D_c(1 - \epsilon_g)}\right)(1 - z)\right] - \frac{u_L L}{D_c(1 - \epsilon_g)}}{\frac{L}{D_c} \left[u_{cs} - \frac{u_L}{1 - \epsilon_g} \right]}$$

In these equations, the two parameters are D_c and u_{cs} .

1. Calculation of D_c (Kato, et al. 1972)

$$\frac{u_G d_R}{D_c} = \frac{13 Fr}{1 + 8Fr^{0.85}}$$

u_G = gas superficial velocity

d_R = reactor column diameter

$$Fr = \text{Froude number, } = \frac{u_G}{(g d_R)^{0.5}}$$

2. Calculation of the settling velocity in a particle swarm,

$$u_{cs} = 1.2 u_{st} \left(\frac{u_G}{u_{st}} \right)^{0.25} \left(\frac{1 - \epsilon_s^*}{1 - \epsilon_{s1}^*} \right)^{2.5}$$

u_{st} = terminal settling velocity according to Stoke's Law

ϵ_s^* = volume fraction of solids in the bubble free suspension

ϵ_{s1}^* = the value of ϵ_s^* at 0.1 g/cm³ solids conc.

3. To calculate u_{st}

$$Re = \frac{u_{st} d_p}{\nu}$$

d_p = particle diameter

ν = kinematic viscosity of the liquid

$$Re = \frac{Ar}{18} \quad \text{if } Re \leq 0.5$$

$$Re = \left(\frac{Ar}{13.9} \right)^{0.7} \quad \text{if } Re > 0.5$$

where Ar is the Archimedes number given by

$$Ar = \frac{\rho_L (\rho_{cat} - \rho_L) g d_p^3}{\mu_L^2}$$

ρ_L - liquid density

ρ_{cat} - catalyst density (particle density)

μ_L - fluid viscosity

With the knowledge of D_c and u_{cs} , the solids (catalyst) concentration profile in a suspension reactor can be calculated for various operating conditions (u_G , u_L , d_R , etc.). This information is important for process optimization and yield estimation.

Validity of the sedimentation dispersion model was confirmed by several investigators. At low Froude numbers and for large particle diameters Kato et al. (1972) observed significant deviation from the equation

$$\frac{u_G d_R}{D_c} = \frac{13 Fr}{1 + 8 Fr^{0.85}}$$

which can be accounted for by incorporating the particle Reynolds number in the correlation. However, this should not be necessary for F-T Synthesis' and Methanol Synthesis Reaction. So, for these cases

$$\frac{u_G d_R}{D_c} = \frac{13 Fr (1 + 0.009 Re_p Fr^{-0.8})}{1 + 8 Fr^{0.85}}$$

Thus, in the equations presented on page 12, the R_A terms should be multiplied by C_{cat} to get the real profiles.

F. Calculation of the Transport Parameters

As we have shown already, of the mass transfer coefficients, we only need $k_L A$ since $k_s a_p \gg k_L a$. In addition we need the gas and the liquid holdup, the axial dispersion coefficient D_L and the relevant parameters in the correlations.

1. Axial Dispersion Coefficient:

Ref: Y. T. Shah and W. D. Deckwer, Scale-up Aspects of Fluid-Fluid Reactions, in "Scale-up in Chemical Process Industries",

R. Kabel and A. J. Bisio, Editors, Wiley, New York, 1986.

For non-flowing liquid phase (batch slurry with gas flow) they give

$$\frac{u_G L}{D_L \epsilon_L} = 2.83 \left(\frac{u_G^2}{g d_R} \right)^{0.34}$$

u_G - mean linear gas velocity

D_L - axial dispersion coefficient

L - column length

ϵ_L - liquid holdup = $1 - \epsilon_G$.

g - acceleration of gravity, 980 cm/s^2

d_R - column diameter.

Another correlation is

$$D_L = 3.676 u_G^{0.32} d_R^{1.34} \text{ cm}^2/\text{s}$$

in this equation u_G is in cm/s d_R in cm .

2. The Mass Transfer Coefficient, $k_L a$

Some authors (for example Alvarez-Cuenca et al., 1980) have reported the dependence of $k_L a$ on the liquid flow rate. However, it has been shown by Barckhart and Deckwer (1976) that this effect results from using the NTU method for the data evaluation, which assumes plug flow for both phases in a bubble column.

There are numerous correlations in the literature to determine $k_L a$. Most widely accepted ones are given below.

a. Akita and Yoshida, 1973

Ref: Akita, K., F. Yoshida, Ind. Eng. Chem., Process Des. Dev., 12, 76(1973).

$$\frac{(k_L a)_A d_R^2}{D_A} = 0.6 \left[\frac{\nu_L}{D_A} \right]^{0.5} \left[\frac{g d_R^2 \rho_L}{\sigma_L} \right]^{0.62} \left[\frac{g d_R^3}{\nu_L^2} \right]^{0.31} \left[\epsilon_G \right]^{1.1}$$

d_R = column diameter

D_A = diffusion coefficient of A in the liquid

ν_L = kinetic viscosity of the liquid

ρ_L = liquid density

g = gravitational constant

σ_L = surface tension

ϵ_G = gas hold up.

Alvarez-Cuenca, M., G. C. J. Baker, M. A. Bergougnou, Chem. Eng. Sci., 35, 1121 (1980)

Barckhart, R., W. D. Deckwer, Verfahrenstechnik (Mainz), 10, 429 (1976).

b. Calderbank and Moo-Young (1961)

Ref: Calderbank, P. M., M. B. Moo-Young, Chem. Eng. Sci., 16, 39 (1961)

$$k_L = 0.42 \left[\frac{(\rho_L - \rho_G) \mu_L g}{\rho_L^2} \right]^{1/3} \left[\frac{D_A \rho_L}{\mu_L} \right]^{1/2}$$

ρ_G - gas density

ρ_L - liquid density

μ_L - liquid viscosity

D_A - diffusion coefficient

g - gravitational constant

To use this equation, one needs the interface area "a" to calculate $k_L a$.

Calderbank, in Trans. Instr. Chem. Eng., 36, 443 (1958) gives "a" as

$$a = 1.44 \frac{\left(\frac{P}{V_L} \right)^{0.4} \rho_L^{0.2}}{\sigma_L^{0.6}} \left(\frac{u_g}{u_t} \right)$$

P - power consumption in agitation, V_L - slurry volume

u_g - gas superficial velocity, u_t - terminal bubble velocity.

limitations of the correlation for "a" are given in the original reference.

There are other ways of interpreting the gas-liquid interface area.

$$a = 6 \frac{\epsilon_G}{d_m}$$

ϵ_G - gas holdup

d_m - volume/surface mean bubble diameter.

(or also sauter mean diameter)

Deckwer, et al., Ind. and Eng. Chem. Process Des. Dev., 21, 231 (1982)

$$\text{give } a = 4.5 u_g^{1.1}$$

Akita and Yoshida, Ind. Eng. Chem. Process Des. Dev., 13, 84 (1974),

give

$$a d_R = \frac{1}{3} \left[\frac{g d_R^2 \rho_L}{\sigma_L} \right]^{0.5} \left[\frac{g d_R^3}{\nu_L^2} \right] \left[\epsilon_G \right]^{1.13}$$

C. Kawagoe, et al. Correlation

Kawagoe, M., K. Nakao, T. Otake, J. Chem. Eng. Japan, 8, 254 (1975).

$$\frac{k_L d_m}{D_A} = 0.975 \left[\frac{\mu_L}{D_A \rho_L} \right]^{1/2} \left[\frac{g d_m^3 \rho_L^2}{\mu_L^2} \right]^{1/4}$$

This correlation, again needs a , the interface area and an expression for the mean bubble diameter.

D. Deckwer, et al., 1983

Deckwer, W. D., K. Nguyen-tein, B. G. Kelkar, Y. T. Shah, AIChE J., 29, 915 (1983).

$$k_L a = 0.467 u_g^{0.82} \quad \text{where } u_g \text{ is in m/s}$$

The first two correlations, Akita and Yoshida and Calderbank and Moo

Young are the ones used the most. It has been pointed out that the correlation of Akita and Yoshida applies well to the cases where gas is sparged by less effective spargers, i.e., either single or multi orifice distributors. Therefore, the Akita-Yoshida correlation can be recommended for a conservative estimation of $k_L a$. Only Margartz and Pilhofer (Chem. Eng. Sci., 36 1069 (1981)) report even lower $k_L a$ values, i.e. about 50% of those predicted from Akita & Yoshida Correlation. If efficient gas spargers like porous plates and two component nozzles are used $k_L a$ values, considerably higher than those calculated from the correlation of Akita and Yoshida can be obtained.

In slurry bubble columns $k_L a$ is affected by the presence of solids. The degree of influence depends on the particle concentration, size, the liquid-solid density difference, geometric shape, and operating condition.

At high liquid velocities ($u_L = 0.093$ m/s) and low gas velocities, the $k_L a$ values are slightly higher than those without the presence of solids. Such a small increase in $k_L a$ is reported by various investigators at low particle concentration, typically less than 15%, for particle sizes in the 50 - 300 micron range.

References:

1. Nguyen-Tien, K., W. D. Deckwer, Chem. Eng. Sci., 17, 693 (1962).
2. Joosten, G. E. H., J. G. H. Schilder, J. J. Jansen, Chem. Eng. Sci., 22, 563 (1977).
3. Slessor, C. G. M., W. T. Allen, A. R. Cummings, U. Pavlowsky, J. Shields, Chem. Reaction Eng., Proc. 4th European Symposium, Brussels, 41, 1968.

4. Tamhaukar, S. S., R. V. Chaudhari, Ind. Eng. Chem., Fundam 18, 406 (1979).

With rising gas velocities and decreasing liquid velocities the $k_L a$ values are lower than those obtained without the dispersed solid phase. At high solid concentration, a steep decrease in $k_L a$ takes place which is caused by a decrease in "a".

Ref. - Kato, Y., A. Nishiwaki, T. Kago, T. Fukuda, S. Tarraha, Int. Chem. Eng. 13, 582 (1973).

Joosten, et al. has shown that as solids are added to the bubble column $k_L a$ first increases slightly and then starts to decrease rapidly by addition of more solids. The point (or solids conc.) where the decrease starts depends on the solid type and particle size. The curves of $k_L a$ v.s. volume fraction of solids, therefore, do not coincide for various solids and particle sizes. They explain the sharp reduction in $k_L a$ by reduction in the interface area "a". They had observed that the gas holdup at high solids concentration (greater than 15%) is lower and gas bubbles are larger, apparently bubble coalescence takes place at a higher frequency.

Joosten et al. as well as Deckwer and co-workers claim that presence of solid particles in the range $50 < d_p < 200$ microns and at loadings less than 15%, the effect of solids on $k_L a$ is negligible.

However, we know that even then, the process of mass transfer can be enhanced if the particles are very reactive or if the volumetric absorption capacity of the particles with respect to A (the absorbing species) is much larger than the solubility of A in the liquid.

Recently, new data reported (Sada, et al., Chem. Eng. Sci., 38

2047 (1983)), indicates 50% drop in $k_L a / k_L a^0$ with 10% solids loading of 2 micron particles ($k_L a^0$ is the mass transfer in absence of solids).

An equation predicting the drop in $k_L a$ is still missing.

Effects of Solids on $K_L a \approx k_L a$

- It is shown in the literature that $k_L a$ decreases with loading of solid catalyst in the slurry, especially in the loading range above 15%. References are provided in the previous report.
- From a fundamental point of view, k_L is a property related to a solute diffusing from the interface into the liquid phase. Hence, theoretically k_L should be independent of solute loading. Surface renewal theory gives $k_L \propto \sqrt{D_A}$.

The solids loading, however, will change the interphase area "a" since they will affect both the bubble size and the bubble coalescence.

If we start with the Akita-Yoshida correlation

$$\frac{(k_L a) d_R^2}{D_A} = 0.6 \left(\frac{v_L}{D_A} \right)^{0.5} \left(\frac{g d_R^2 \rho_L}{\sigma_L} \right)^{0.62} \left(\frac{g d_R^3}{v_L^2} \right)^{0.31} (\epsilon_G)^{1.1}$$

and calculate $(k_L a) / (k_L a)^0$ where $(k_L a)^0$ is the mass transfer coefficient in the absence of solids, we get

$$\frac{k_L a}{(k_L a)^0} = \left(\frac{v_L}{v_L^0} \right)^{0.5} \left[\left(\frac{\rho_L}{\sigma_L} \right) \left(\frac{\sigma_L^0}{\rho_L^0} \right) \right]^{0.62} \left(\frac{v_L^0}{v_L} \right)^{0.62} \left(\frac{\epsilon_G}{\epsilon_G^0} \right)^{1.1}$$

since $v_L = \frac{\mu_L}{\rho_L}$; and d_R, D_A, g are constants and if we assume $\sigma_L = \sigma_L^0$ in absence

of data on the effect of solids on surface tension, one obtains a correction factor CF such that CF multiplied by $(k_L a)^0$ from Akita-Yoshida Equation yields the $k_L a$ for the slurry. Thus

$$C.F. = \frac{k_L a}{(k_L a)^0} = \left(\frac{\mu_L^0}{\mu_L} \right)^{0.12} \left(\frac{\rho_L}{\rho_L^0} \right)^{0.74} \left(\frac{\epsilon_G}{\epsilon_G^0} \right)^{1.1}$$

In this equation, ρ_L is the density of the slurry.

$\rho_L = \epsilon_s \rho_s + (1 - \epsilon_s) \rho_L^0$ where ρ_s is the density of solids, ϵ_s is the volume fraction of solids, and ρ_L^0 is the density of pure liquid.

$$\therefore \frac{\rho_L}{\rho_L^0} = \epsilon_s \frac{\rho_s}{\rho_L^0} + (1 - \epsilon_s)$$

One of the better equations for predicting ϵ_G in presence of solids is proposed by Zheng, et al. Reference: Zheng, L., B. Yao, Y. Feng, *Chem. Eng. Sci.*, 43, 2195 (1988).

They give

$$\epsilon_G = 0.114 Fr^{0.35} Ar^{0.11} \left(1 + \frac{u_L}{u_G}\right)^{-0.48} (1 - \epsilon_s)^{1.74}$$

$$\text{where: } Fr = \frac{u_G}{\sqrt{g d_R}}$$

$$Ar = \frac{g d_p^3 \rho_L (\rho_s - \rho_L)}{\mu_L^2}$$

$$\text{Then: } \left(\frac{\epsilon_G}{\epsilon_G^0}\right) = (1 - \epsilon_s)^{1.74}$$

So the correction factor becomes

$$C.F. = \frac{k_L a}{(k_L a)^0} = \left(\frac{\mu_L^0}{\mu_L}\right)^{0.12} \left(\epsilon_s \frac{\rho_s}{\rho_L^0} + (1 - \epsilon_s)\right)^{0.74} (1 - \epsilon_s)^{1.914}$$

In the above analysis it is assumed that the Froude and Archimedes numbers are the same for the liquid and the slurry in the limit as $\epsilon_s \rightarrow 0$.

The above correlation seems to work for the data in the literature in the particle range ~50 microns. The correlation fails for larger and/or smaller particles due to the significant contribution from the Archimedes number. However, for other diameter particles

$$\frac{(k_L a)_1}{(k_L a)_2} = \frac{(d_{p1}^3)^{0.11}}{(d_{p2}^3)^{0.11}} = \left(\frac{d_{p1}}{d_{p2}}\right)^{0.33} \quad \text{where 1 is for 50 } \mu\text{m, 2 is for other sizes}$$

if everything else is the same.

I have applied the above correlation to Joosten's data and Sada et al.'s data. The results are as follows:

Joosten et al., *Chem. Eng. Sci.*, 32, 563 (1977).

Sada et al., *Chem. Eng. Sci.*, 38, 2047 (1983).

Thus, the equation is:

$$\frac{(k_L a)}{(k_L a)^0} = \left(\frac{\mu_L^0}{\mu_{SL}}\right)^{0.12} \left(\epsilon_s \frac{\rho_s}{\rho_L^0} + (1 - \epsilon_s)\right)^{0.74} (1 - \epsilon_s)^{1.914} \left(\frac{d_p}{50}\right)^{0.31}$$

μ_{SL} - slurry viscosity; d_p - particle diameter in microns

Dispersed Solid	Size	Solids Loading	$(k_L a)$ Measured	$(k_L a)$ Calculated	
Polypropylene	53 – 105 μ	30%	0.08 s ⁻¹	0.079 s ⁻¹	Data from Joosten et al.
		35%	0.04	0.066	"
		40%	–	0.054	"
Polypropylene	250 μ	30%	0.16	0.12	"
		35%	0.13	0.10	"
		40%	0.06	0.08	"
Glass Beads	53 μ	9%	0.20	0.18	"
		30%	0.16	0.12	"
		35%	0.11	0.10	"
		40%	0.06	0.08	"
Glass Beads	88 μ	30%	0.16	0.13	"
		35%	0.14	0.12	"
		40%	0.10	0.09	"
Sugar	74 – 105 μ	30%	0.13	0.11	"
		35%	0.06	0.075	"
		40%	0.04	0.06	"
and from Sada et al.			$k_L a / (k_L a)^0$		
Mg(OH) ₂	2 μ	5%	measured 0.6	– calculated 0.4	

Although the correlation is quite simple to use, and somewhat empirical, it seems to work. The $(k_L a)^0$ from Joosten et al., is 0.2 s⁻¹ in the absence of solids. So the agreement is acceptable.

When I apply the technique to F-T and/or MeOH synthesis, the following results are obtained:

Data: μ_{SL}/μ_L (the liquid viscosity increases with solid content, we assumed the values measured by Joosten et al. since his liquid, kerosene, is similar to the F-T wax and/or MeOH fluid at reaction conditions $\Rightarrow \rho_L = 0.8 \text{ g/cm}^3$, $\mu_L = 1 - 2 \text{ cp.}$)

$$\therefore 25\% \text{ loading } \frac{\mu_{SL}}{\mu_L} = 6.5$$

$$30\% \text{ loading } = 10$$

$$35\% \text{ loading } = 15$$

$$40\% \text{ loading } = 20$$

Skeletal density is taken as 5.5, as specified in Air Products Report p. III-19 – Skeletal density of iron catalyst and it is consistent with values for iron ore reported in Perry's. Particle density ρ_s is taken as 3.3 g/cm³ based on an assumed porosity of 40% (gas filled).

$$\rho_L = 0.8 \text{ g/cm}^3, \quad d_p = 26 \mu$$

Then:

$$\frac{k_L a}{(k_L a)^0} = \left(\frac{\mu^0}{\mu} \right)^{0.12} \left(\epsilon_s \frac{\rho_s}{\rho_L} + (1 - \epsilon_s) \right)^{0.74} (1 - \epsilon_s)^{1.914} \left(\frac{26}{50} \right)^{0.33}$$

Loading Volume %	$[k_L a / k_L^0 a]$ Calculated
25%	0.56
30%	0.50
35%	0.44
40%	0.37

Calculation of $(k_L a)^0$, Akita Yoshida Correlation

$$\frac{(k_L a)^0 d_R^2}{D_A} = 0.6 \left(\frac{\mu_L}{D_A \rho_L} \right)^{0.5} \left(\frac{g d_R^2 \rho_L}{\sigma_L} \right)^{0.62} \left(\frac{g d_R^3 \rho_L}{\mu_L^2} \right)^{0.31} (\epsilon_G)^{1.1}$$

$$\mu_L = 2\text{-}\varphi \Rightarrow \text{Fig. III B-1, page III-22 of Air Products Report}$$

$$\rho_L = 0.8 \text{ g/cm}^3$$

$$\sigma_L = 16.5 \text{ dyne/cm at } 250\text{C, Air Products Rpt. p. III-7}$$

$$\left. \begin{array}{l} D_A \text{ for H}_2 = 54 \times 10^{-5} \text{ cm}^2/\text{s} \\ D_A \text{ for CO} = 20 \times 10^{-5} \text{ cm}^2/\text{s} \end{array} \right\} \text{from our measurements}$$

$$g = 980 \text{ cm/s}^2$$

$$\therefore (k_L a)_{\text{H}_2}^0 = 2.01 d_R^{0.17} \epsilon_G^{1.1}$$

$$(k_L a)_{\text{CO}}^0 = 1.27 d_R^{0.17} \epsilon_G^{1.1}$$

where d_R is the tube diameter in cm., ϵ_G is the gas hold up.

Akita-Yoshida correlation for ϵ_G is:

$$\frac{\epsilon_G}{(1 - \epsilon_G)^4} = 0.2 \left(\frac{g d_R^2 \rho_L}{\sigma_L} \right)^{1/8} \left(\frac{g d_R^3 \rho_L^2}{\mu_L^2} \right)^{1/12} \frac{u_g}{\sqrt{g d_R}}$$

$$\frac{\epsilon_G}{(1 - \epsilon_G)^4} = 0.034 u_G \text{ for the system defined above (note that the } d_R \text{ terms cancels.)}$$

for $u_G = 15 \text{ cm/s} = 0.5 \text{ ft/s}$

$$\epsilon_G = 0.20$$

$$\therefore (k_L a)_H^0 = 0.342 d_R^{0.17}$$

$$(k_L a)_{CO}^0 = 0.216 d_R^{0.17}$$

Thus for the reactor

Volume %	$(k_L a)_H$	$(k_L a)_{CO}$
25% loading	$0.192 d_R^{0.17}$	$0.121 d_R^{0.17}$
30% loading	$0.171 d_R^{0.17}$	$0.108 d_R^{0.17}$
35% loading	$0.150 d_R^{0.17}$	$0.095 d_R^{0.17}$
40% loading	$0.127 d_R^{0.17}$	$0.080 d_R^{0.17}$

These will be the $(k_L a)$ values as a function of d_R . I would like to note that as d_R ranges from 1 cm to 10 m (1000 cm), $d_R^{0.17}$ varies only from 1 to 3.23.

Model Solutions for Slurry Reactors

A. ASSUMPTIONS

1. Gas phase in plug flow
2. Liquid phase not mixed and in PF (Model 1) or perfectly mixed (Model 2)
3. Only gas/liquid mass transfer and the reaction terms are important, liquid/solid mass transfer resistance is negligible
4. Intraparticle diffusion is negligible (small particles, $\eta = 1.0$)
5. First order reaction rate; $r = k_r \epsilon_L C_H$
6. Constant usage ratio (moles of CO consumed per mole H is constant), the stoichiometry is $H_2 + \gamma CO \rightarrow \text{products}$
7. Liquid phase batch
8. Assume catalyst uniformly dispersed

MODEL 1

Gas phase plug flow, liquid phase not well agitated so that the concentration in the liquid phase varies along the reactor as well.

$$- \frac{d(u_G P_H)}{dx} = k_L a \left(\frac{P_H}{H_H} - C_H \right)$$

$P_H = RT C_{GH}$ where C_{GH} is the gas phase concentration

$$\frac{C_{GH}}{H_H} = C_H^* \text{ the interphase concentration}$$

$$P_H = y_H P \Rightarrow \text{ideal gas}$$

$$\therefore - \frac{d(u_G P_H)}{dx} = k_L a RT \left(C_H^* - \frac{C_H}{RT} \right) = k_r \epsilon_L C_H$$

$$\text{For the liquid phase } k_L a RT \left(C_H^* - \frac{C_H}{RT} \right) = k_r \epsilon_L C_H$$

$$\therefore C_H = \frac{k_L a RT C_H^*}{k_r \epsilon_L + k_L a}$$

Substitute back and simplify

$$- \frac{d(u_G y_H)}{dx} = \frac{(k_L a) k_r \epsilon_L RT}{(k_r \epsilon_L + k_L a) P} C_H^*$$

$$\text{let } \frac{1}{K_H} = \frac{1}{k_L a} + \frac{1}{k_r \epsilon_L} \quad , \quad C_H^* = \frac{y_A P}{H_H} \quad , \quad z = \frac{x}{L}$$

$$\therefore - \frac{d(u_G y_H)}{dz} = \frac{K_H R T L}{H_H} y_H$$

$$\text{define conversion } X_H = \frac{u_{G0} y_{H0} - u_G y_H}{u_{G0} y_{H0}}$$

$$\text{then } u_G y_H = u_{G0} y_{H0} (1 - X_H)$$

Overall conversion (H and CO combined)

$$X_{H+CO} = X_H \frac{1+U}{1+I} \quad \text{where } U = \frac{\text{change in \# of moles of CO}}{\text{change in \# of moles of H}}$$

$$\text{inlet ratio } I = \frac{n_{CO}^0}{n_H^0} \quad , \quad \text{ratio of inlet molar flow rates}$$

$$u_G = u_{G0} (1 + \alpha X_{CO+H}) \quad \text{where } \alpha \text{ is contraction factor defined as}$$

$$\alpha = \frac{Q \text{ (at } X_{H+CO} = 1) - Q_0}{Q_0} \quad , \quad Q \text{ is the volumetric flow rate}$$

$$\text{then } d(u_G y_H) = - u_{G0} y_{H0} dX_H$$

$$\frac{y_H}{u_G} = \frac{u_{G0} y_{H0} (1 - X_H)}{u_G} = \frac{y_{H0} (1 - X_H)}{(1 + \alpha X_H \frac{1+U}{1+I})}$$

$$\text{let } \alpha^* = \alpha \frac{1+U}{1+I}$$

$$\text{then } u_G^0 y_H^0 \frac{dX_H}{dz} = \frac{K_H R T L}{H_H} y_H^0 \frac{(1 - X_H)}{(1 + \alpha^* X_H)}$$

$$\frac{(1 + \alpha^* X_H)}{(1 - X_H)} \frac{dX_H}{dz} = \frac{K_H R T L}{H_H u_G^0}$$

integrate from 0 to X_H on dX_H
and 0 to 1 on dz

$$(1 + \alpha^*) \ln(1 - X_H) + \alpha^* X_H = -St$$

when the Stanton No $St = \frac{K_H RTL}{u_G^0 H_H}$

Reference: Deckwer, W. D., Serpemen Y., Ralek M., Schmidt, B. *Chem. Eng. Sci.*, 36, 765 (1981).

$$K_H = \frac{(k_L a) (k_r \epsilon_L)}{(k_L a) + (k_r \epsilon_L)}$$

Most studies indicate $\alpha \approx -0.5$

$k_r = k_w W$ where k_w is the rate constant in

units $\frac{\text{volume}}{\text{mass catalyst} \times \text{time}}$ and W is

catalyst loading in $\frac{\text{mass}}{\text{unit volume}}$

At this stage we may take into consideration the change in ϵ_G and u_G in calculating $(k_L a)$ from Akita-Yoshida correlation.

$$\frac{\epsilon_G}{(1 - \epsilon_G)^4} = 0.034 u_G \quad (\text{p. 3 of previous report})$$

and $(k_L a) \propto \epsilon_G^{1.1}$

so $u_G = u_{G0} (1 + \alpha X_{CO+H})$

Solution of this equation, X_H vs. St will give the conversion profile. In the Stanton number $k_L a$ and L are variables.

MODEL 2

Gas phase in plug flow, liquid phase perfectly mixed.

Gas phase – using concentration instead of partial pressure.

$$- \frac{d(u_G C_{HG})}{dx} = k_L a (C_{HL}^* - C_{HL})$$

Liquid Phase

$$A_c \int_0^L k_L a (C_{HL}^* - C_{HL}) dx = V k_L a C_{HL}, \quad V \text{ is the volume of the slurry}$$

Based on previous definition

$$C_{HG} = C_{HG}^0 \left(\frac{1 - X_H}{1 + \alpha^* X_H} \right)$$

$$u_G = u_G^0 (1 + \alpha^* X_H)$$

Alternatively, we can use overall hydrogen balance

$$u_G^0 A_c C_{HG}^0 X_H = k_L a C_{HL} V$$

Substituting these back into the first equation and integrating as before, we get:

$$\frac{L(k_L a)}{u_G^0 H_H} = - \frac{1}{1 + \alpha^* n} \left(\alpha^* X_H + (1 + \alpha^* Y) \ln \left(1 - \frac{X_H}{Y} \right) \right)$$

$$\text{where } n = \frac{H_H C_{HL}}{C_{HG}^0} \quad Y = \frac{1 - n}{1 + \alpha^* n}$$

Rearranging the overall hydrogen balance

$$\frac{A_c X_H u_G^0}{(k_L a) V} = \frac{X_H u_G^0}{(k_L a) L} = \frac{C_{HL}}{C_{HG}^0}$$

Multiply by X_H

$$\frac{X_H u_G^0 H_H}{k_L a L} = \frac{H_H C_{HL}}{C_{HG}^0} = n$$

\therefore We have an implicit relationship between X_H and $\frac{L(k_L a)}{u_G^0 H_H}$

Reference: Bukur, D., Chem. Eng. Sci. 33, 441 (1988).

The liquid phase mixing and volume contraction (α) have a very significant effect on the reactor performance, particularly at high conversion. For example, if 90% hydrogen conversion is desired, the required reactor heights calculated from these two models are:

1. 8.3 m Model 1 $\alpha = -0.5$
2. 17 m Model 1 $\alpha = 0$
3. 23.3 m Model 2 $\alpha = -0.5$
4. 63.1 m Model 2 $\alpha = 0$

Thus axial mixing, D_z , and volume contraction factor, α , are very important. PF model, Model 1, assumes $D_z = 0$ and PM model, Model 2, assumes $D_z = \infty$.

The above numbers are from Bukur's paper. When we have a non first order reaction rate expression and axial mixing term D_z , the numbers calculated will be somewhat in the middle.

Effectiveness Factors in Fixed-Bed Fischer Tropsch

It is generally agreed that in F-T synthesis in the gas phase, the catalyst pores will be wax filled.

Excellent reference is Huff and Satterfield, Ind. Eng. Chem., Process Des. Dev., 24, 986 (1985).

If we assume liquid filled pores, Avg. MWt of wax = 400, then 1/8" - 1/16" diameter particles with 1st order rate constant $0.01 - 0.4 \text{ s}^{-1}$, then from

$$\theta = \frac{R}{3} \sqrt{k/D} \quad \text{with } D = 50 \times 10^{-5} \text{ cm}^2/\text{s}$$

we get $\theta = 0.11 - 1.44$

and $\eta = 1.0 - 0.62$

Similarly for CO, $\eta = 1.0 - 0.42$

So the diffusion effect will not be very large.