CSIR REPORT CENG 581

MULTICOMPONENT MODELLING
OF FISCHER-TROPSCH SLURRY REACTORS

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CHEMICAL ENGINEERING RESEARCH GROUP

COUNCIL for SCIENTIFIC and INDUSTRIAL RESEARCH

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S Y N O P S I S

In the multicomponent model developed for a Fischer-Tropsch slurry reactor, the water-gas shift reaction is assumed to be in equilibrium. This is supported by literature data on iron-based catalysts above 523 K and synthesis gas conversion above ~ 50 %. A Schulz-Flory product distribution is used.

Investigation of the effects of back-mixing and interphase mass transfer using the model shows that, although the mass transfer rates in full-scale reactors are fast compared with reaction rates, the ratio of the mass transfer rates of reactants and products is important in determining gas velocity and gas hold-up and hence reactor performance.

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MULTIKOMPONENTMODELLERING VAN
FISCHER-TROPSCH FLODDERREAKTORS

D S VAN VUUREN   Augustus 1985
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SINOPSIS

In die ontwikkelde multikomponentmodel vir 'n Fischer-Tropsch flodderreaktor word aangeneem dat die watergasreaksie in ewewig is. Die aanname word deur die literatuur oor ysterkatalisators bo 523 K en met 'n sintesegasomsetting bo ~ 50 % bevestig. Vir die produksamestelling word 'n Schulz-Flory verdeling gebruik.

'n Ondersoek van terugmenging en massa-oordrag tussen gas en vloeistof, met gebruikmaking van die model, het gewys dat, hoewel die massa-oordrag in volskaalse reaktors vinnig is in vergelyking met die reaksiesnelheid, die verhouding tussen die massa-oordragstempo's van reaktante en produkte belangrik is, omdat dit die gassnelheid en die gasfraksie en daardeur ook die reaktoreffektiwiteit beïnvloed.

C O N T E N T S

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1.   INTRODUCTION

Bubble column slurry reactors are an alternative to the fixed-bed or entrained-bed reactors used in the industrial-scale application of Fischer-Tropsch (F-T) synthesis. In recent reviews[1,2] the main merits of slurry reactors for this purpose were pointed out to be:

-    excellent temperature control (heat transfer from a liquid)
-    simple mechanical construction
-    ability to accept a synthesis gas with a low H_2:CO ratio
-    flexible product spectra.

The major disadvantage is lower space-time yields for the same catalyst. However, the potential for superior heat removal makes it possible to use catalysts of high activity compared with those currently used in industrial practice.

In order to understand the interrelation between the physical and chemical processes occurring in slurry reactors and to design and optimize full-scale reactors, a realistic model is required. Calderbank et al.[3] assumed that both the gas and liquid phases are in plug flow, that the liquid flow rate is negligible, and that the reaction rate is first order with respect to the hydrogen concentration. They measured the fluid physical properties separately from the reaction experiments and concluded that both the intrinsic reaction rate and the hydrogen gas-liquid interfacial mass transfer rate are important in determining reactor performance.

Satterfield and Huff[4] derived a model assuming the liquid phase to be perfectly mixed and the gas phase in plug flow. The synthesis gas consumption rate (H_2 plus CO) was assumed to be first order with respect to hydrogen. They analysed data given by Schlesinger et al.[5] and concluded that the hydrogen gas-liquid interfacial mass transfer becomes important at elevated temperatures.

Deckwer et al.[6] analysed the same data using a plug flow model for both gas and liquid phases. They refined the model used by Calderbank et al.[3] as follows: the decrease in gas velocity caused by conversion was accounted for by means of a constant contraction factor, and the consumption ratio of H_2:CO was assumed to be constant throughout the reactor. In contrast to previous workers, they concluded that the hydrogen gas-liquid interfacial mass transfer is negligible in F-T slurry reactors. This was the result of different assumptions about the gas-liquid interfacial area. In a later paper, Quicker and Deckwer[7] presented supporting experimental data.

Bukur[8] and Van Vuuren[9] used the refinements introduced by Deckwer (constant gas contraction and constant H_2:CO consumption ratio) but assumed the gas to be in plug flow and the liquid to be perfectly mixed.

In the meantime Deckwer et al.[10] had derived and used an axial dispersion single-component model to estimate the performance of large-scale F-T slurry reactors. Non-isothermal conditions, intraparticle mass transfer, liquid-solid mass transfer and non-uniform catalyst concentration profiles were incorporated, together with a constant gas contraction factor and H_2:CO consumption ratio. Whereas the models discussed previously yielded algebraic solutions, this model required numerical methods. The analysis indicated that the liquid-solid mass transfer resistance and the catalyst settling rate need not be taken into account.

Stern et al.[11] were the first to use a multicomponent model to analyse mass transfer effects in F-T slurry reactors. They assumed the gas phase to be in plug flow and the liquid phase to be perfectly mixed. The gas velocity change is accounted for by considering the gas-liquid interphase mass transfer of all the reactants and products. They applied their model to four-component reactions, such as the methanation reaction, and concluded that, although the hydrogen mass transfer resistance may be negligible, the ratio of H_2:CO mass transfer rates can cause a high H_2:CO concentration ratio in the liquid phase. In turn, this may influence the average molecular mass of the product formed and the olefin to paraffin ratio in the product.

The ability of slurry reactors to process synthesis gas of low H_2:CO ratios was explained by Satterfield and Huff[12] in terms of the large degree of back-mixing in slurry reactors, the water-gas shift activity of F-T catalysts and the high synthesis gas conversion. This effect, and also the stoichiometry of the F-T reaction and the dependence of the intrinsic reaction rate on the concentrations of H_2O and CO, have not yet been incorporated into advanced slurry reactor models.

The purpose of the present study is to test the simplifying assumptions made by previous workers by means of a suitable model. Effects such as variation of the gas contraction factor and the H_2:CO usage ratio are investigated. The two limiting cases for the liquid phase, perfect mixing and no mixing, are considered. Finite rates of mass transfer are included in the two models: the gas plug flow, perfectly mixed liquid phase model (PMF model), and the gas plug flow, non-mixed liquid phase model (PPF model).

The limit of no mass transfer resistance is derived for the PMF model in the form of an algebraic equation which allows rapid estimation of the reactor performance without having to resort to simplified single-component models. An algebraic equation is also derived for calculating the overall H_2:CO usage ratio.

2. MODELS

In the models derived here the following assumptions have been made:

- the gas phase is in plug flow;
- the products are mainly alkanes;
- the products have a Schulz-Flory (S-F) distribution; and
- the catalyst has sufficient water-gas shift activity for this reaction to be in equilibrium throughout the reactor.

2.1 Gas plug flow; perfectly mixed liquid phase (PMF model)

This model is an extension of the model derived by Stern et al.[11]. In the numerical examples four inorganic reacting compounds, H_2, CO, H_2O and CO_2, and ten alkane products up to decane are taken into account. However, the model does not place a restriction on the number of alkanes that can be used.

The gas phase mass balance equation for each component, written for a differential reactor element, is

$$-\frac{d(U_G C_{G,i})}{dz} = k_{L,i} a \left(\frac{C_{G,i}}{m_i} - C'_{L,i} \right) \tag{1}$$

The overall mass balance for the gas phase is

$$-C_G \frac{dU_G}{dz} = \Sigma k_{L,i} a \left(\frac{C_{G,i}}{m_i} - C_{L,i} \right) \tag{2}$$

The boundary conditions of Equations (1) and (2) at $z = 0$ are:

$$U_G = U_G^o \quad \text{and} \quad C_{G,i} = C_{G,i}^o.$$

When no reactants or products enter the reactor in the liquid phase, the liquid phase mass balance for each component is:

$$-Q_L C_{L,i} + \int_o^V k_{L,i} a \left(\frac{C_{G,i}}{m_i} - C_{L,i} \right) dV = V(1 - \epsilon)wr_i \tag{3}$$

This can be written as:

$$-Q_L C_{L,i} + V k_{L,i} a \left(\frac{\overline{C}_{G,i}}{m_i} - C_{L,i} \right) = Vw(1 - \varepsilon) r_i \tag{4}$$

where
$$\overline{C}_{G,i} = \frac{1}{V} \int_0^V C_{G,i} \, dV \tag{5}$$

These equations can be written in dimensionless form (Stern et al.[11]) using the following definitions:

$$\theta_{G,i} = \frac{C_{G,i}}{C_{G,H_2}^o}, \qquad \nu = \frac{U_G}{U_G^o}$$

$$\theta_{L,i} = \frac{C_{L,i} m_i}{C_{G,H_2}^o}, \qquad \omega_G = \frac{U_G^o}{L}$$

$$\theta_G = \frac{C_G}{C_{G,H_2}^o}, \qquad \omega_L = \frac{Q_L}{V},$$

$$\zeta = \frac{z}{L} \qquad \text{and} \qquad N_i = \frac{k_{L,i} aL}{m_i U_G^o}$$

The resulting dimensionless equations are:

$$-\frac{d(\nu \theta_{G,i})}{d\zeta} = N_i(\theta_{G,i} - \theta_{L,i}) \tag{6}$$

$$-\theta_G \frac{d\nu}{d\zeta} = \Sigma N_i(\theta_{G,i} - \theta_{L,i}) \tag{7}$$

$$\overline{\theta}_{G,i} = \int_0^1 \theta_{G,i} \, d\zeta \tag{8}$$

and
$$-\frac{\omega_L}{\omega_G} \theta_{L,i} + N_i m_i(\overline{\theta}_{G,i} - \theta_{L,i}) = \frac{m_i w(1 - \varepsilon) r_i}{\omega_G C_{G,H_2}^o} \tag{9}$$

The boundary conditions at $\zeta = 0$ are:

$$\theta_{G,i} = \frac{C_{G,i}^o}{C_{G,H_2}^o}$$

and $\quad \nu = 1$

To solve Equations (6) to (9) the reaction rate and the stoichiometry of the F-T reaction must be known. Satterfield and Huff[13] measured the reaction rate of the F-T reaction over an iron catalyst in a well-stirred slurry reactor and recommended

$$r_{H_2 + CO} = \frac{k_{FT} b p_{CO} p_{H_2}^2}{p_{H_2O} + b p_{CO} p_{H_2}} \tag{10}$$

In terms of the dimensionless liquid-phase reactant concentrations, this becomes:

$$r_{H_2 + CO} = \frac{k_{FT} b \theta_{L,CO} \theta_{L,H_2}^2 (C_{G,H_2}^o RT)^2}{\theta_{L,H_2O} + b \theta_{L,CO} \theta_{L,H_2} (C_{G,H_2}^o RT)} \tag{11}$$

Equation (11) gives the rate of consumption of synthesis gas, but to solve Equations (6) to (9) the individual consumption rates for H_2 and CO and the individual rates of formation of H_2O and CO_2 are required. These rates also depend on the rate of the water-gas shift reaction, but for iron-based catalysts this reaction may be assumed to be in equilibrium[12,14]. Then

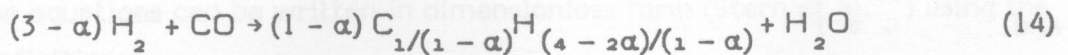$$\frac{\left(m_{CO_2} C_{L,CO_2} RT\right)\left(m_{H_2} C_{L,H_2} RT\right)}{\left(m_{CO} C_{L,CO} RT\right)\left(m_{H_2O} C_{L,H_2O} RT\right)} = K_w \tag{12}$$

The validity of the assumption will be examined later.

In terms of the dimensionless liquid concentrations,

$$K_w = \frac{\theta_{L,CO_2} \theta_{L,H_2}}{\theta_{L,CO} \theta_{L,H_2O}} \qquad (13)$$

The average stoichiometry of the synthesis reaction (without the water-gas shift reaction) when only alkanes are formed, with a S-F distribution, is[15]:

$$(3 - \alpha) H_2 + CO \rightarrow (1 - \alpha) C_{1/(1 - \alpha)} H_{(4 - 2\alpha)/(1 - \alpha)} + H_2O \qquad (14)$$

The stoichiometry of the water-gas shift reaction is:

$$CO + H_2O \leftrightharpoons CO_2 + H_2 \qquad (15)$$

If n_1 is the rate of consumption of CO via the synthesis reaction and n_2 the rate of consumption of CO via the water-gas shift reaction, the reaction rates of the various inorganic components are:

$$r_{H_2} = (3 - \alpha)n_1 - n_2 \qquad (16a)$$

$$r_{CO} = n_1 + n_2 \qquad (16b)$$

$$r_{H_2O} = -n_1 + n_2 \qquad (16c)$$

and

$$r_{CO_2} = -n_2 \qquad (16d)$$

Therefore $r_{H_2 + CO} = r_{H_2} + r_{CO} = (4 - \alpha)n_1 \qquad (17)$

and from Equation (9)

$$r_{CO_2} = \frac{\omega_G \, C^o_{G,H_2}}{m_{CO_2} w(1 - \varepsilon)} \left(N_{CO_2} m_{CO_2} (\bar{\theta}_{G,CO_2} - \theta_{L,CO_2}) - \frac{\omega_L}{\omega_G} \theta_{L,CO_2} \right) \qquad (18)$$

Substituting Equations (16a) to (16d) and Equation (17) into Equation (9) gives:

$$-\frac{\omega_L}{\omega_G} \theta_{L,H_2} + N_{H_2} m_{H_2} (\bar{\theta}_{G,H_2} - \theta_{L,H_2})$$

$$= \frac{m_{H_2} w(1-\varepsilon)}{\omega_G C_{G,H_2}^0} \left(\frac{3-\alpha}{4-\alpha} r_{H_2+CO} + r_{CO_2} \right) \qquad (19)$$

$$\frac{-\omega_L}{\omega_G} \theta_{L,CO} + N_{CO} m_{CO} \left(\overline{\theta}_{G,CO} - \theta_{L,CO} \right)$$

$$= \frac{m_{CO} w(1-\varepsilon)}{\omega_G C_{G,H_2}^0} \left(\frac{r_{H_2+CO}}{4-\alpha} - r_{CO_2} \right) \qquad (20)$$

and $\qquad \dfrac{-\omega_L}{\omega_G} \theta_{L,H_2O} + N_{H_2O} m_{H_2O} \left(\overline{\theta}_{G,H_2O} - \theta_{L,H_2O} \right)$

$$= \frac{m_{H_2O} w(1-\varepsilon)}{\omega_G C_{G,H_2}^0} \left(\frac{-r_{H_2+CO}}{4-\alpha} - r_{CO_2} \right) \qquad (21)$$

The rate of formation of each hydrocarbon species is:

$$-r_{C_n} = \frac{(1-\alpha)^2 \alpha^{i-1}}{4-\alpha} r_{H_2+CO} \qquad (22)$$

Substitution into Equation (9) gives:

$$\frac{-\omega_L}{\omega_G} \theta_{L,C_n} + N_{C_n} m_{C_n} \left(\overline{\theta}_{G,C_n} - \theta_{L,C_n} \right)$$

$$= \frac{m_{C_n} w(1-\varepsilon)(1-\alpha)^2 \alpha^{n-1} r_{H_2+CO}}{\omega_G C_{G,H_2}^0 (\alpha-4)} \qquad (23)$$

Equations (6–8), (13), (18–21) and (23) must be solved simultaneously to predict the reactor performance.

The fraction of the total number of molecules leaving the reactor that are hydrocarbons with a carbon number greater than n is:

$$E = \sum_{i=n+1}^{\infty} \frac{(1-\alpha)^2 \alpha^{i-1} X_{CO+H_2}}{(4-\alpha) - 2X_{CO+H_2}} = \frac{(1-\alpha)\alpha^n X_{CO+H_2}}{(4-\alpha) - 2X_{CO+H_2}} \qquad (24)$$

The maximum error in the gas flow rate caused by neglecting the hydrocarbons with a carbon number greater than n occurs at total conversion of the synthesis gas:

$$E = \frac{(1-\alpha)\alpha^n}{(2-\alpha)} \qquad (25)$$

The chain-growth probability where the error is maximized is:

$$\alpha_m = \frac{(3n+1) - \sqrt{(3n+1)^2 - 8n^2}}{2n} \qquad (26)$$

At α_m neglecting hydrocarbons heavier than decane causes a maximum error of 3,2 % at total conversion of the synthesis gas. The error drops to 2,2 % at 90 % gas conversion and optimum chain-growth probability for production of the diesel fraction ($\alpha = 0,873$). This error is well below that expected from the assumptions made and from the approximations used to calculate the reactor parameters. However, the model allows the use of higher values of n, and the error can thus be reduced.

2.2 Gas plug flow; no mixing in the liquid phase (PPF model)

For these conditions the differential gas-phase mass balance is the same as in the PMF model. The equations can be reduced to

$$\frac{-d\theta_{G,i}}{d\zeta} = \frac{1}{\nu} N_i \left(\theta_{G,i} - \theta_{L,i}\right) - \frac{\theta_{G,i}}{\theta_G \nu} \sum_{i=1}^{\infty} N_i \left(\theta_{G,i} - \theta_{L,i}\right) \qquad (27)$$

Because the liquid phase is not mixed and because its nett flow rate is assumed to be negligible:

$$N_i \left(\theta_{G,i} - \theta_{L,i}\right) = \frac{w(1-\varepsilon)}{\omega_G C^o_{G,H_2}} r_i \qquad (28)$$

From the Schulz-Flory stoichiometry it follows that:

$$\sum_{i=1}^{\infty} N_i\left(\theta_{G,i} - \theta_{L,i}\right) = \sum_{i=1}^{\infty} \frac{w(1-\varepsilon)}{\omega_G C^o_{G,H_2}} r_i = \frac{w(1-\varepsilon)}{\omega_G C^o_{G,H_2}} \frac{2}{4-\alpha} r_{H_2+CO} \tag{29}$$

Therefore Equation (27) is equivalent to

$$\frac{-d\theta_{G,i}}{d\zeta} = \frac{1}{\nu} N_i\left(\theta_{G,i} - \theta_{L,i}\right) + \frac{2w(1-\varepsilon)\theta_{G,i} r_{H_2+CO}}{(4-\alpha)\omega_G C^o_{G,H_2}\theta_G \nu} \tag{30}$$

The gradient of the dimensionless gas velocity is

$$\frac{d\nu}{d\zeta} = -\frac{2w(1-\varepsilon) r_{H_2+CO}}{(4-\alpha)\omega_G \theta_G C^o_{G,H_2}} \tag{31}$$

In order to solve Equations (30) and (31), one needs to consider only the four inorganic components (H_2, CO, CO_2 and H_2O) since the effect of the organic products on the changes in the total gas flow rate is taken into account by Equation (31). Note that the concentrations of the hydrocarbon products do not affect the intrinsic rate of conversion of the synthesis gas.

Equation (30) with the boundary condition

$$\theta_{G,i} = C^o_{G,i} / C^o_{G,H_2} \quad \text{at } \zeta = 0$$

must be solved while the following equations are satisfied:

$$N_{H_2}\left(\theta_{G,H_2} - \theta_{L,H_2}\right) - \frac{w(1-\varepsilon)}{\omega_G C^o_{G,H_2}}\left(\frac{3-\alpha}{4-\alpha} r_{H_2+CO} + r_{CO_2}\right) = 0 \tag{32a}$$

$$N_{CO}\left(\theta_{G,CO} - \theta_{L,CO}\right) - \frac{w(1-\varepsilon)}{\omega_G C^o_{G,H_2}}\left(\frac{1}{4-\alpha} r_{H_2+CO} - r_{CO_2}\right) = 0 \tag{32b}$$

$$N_{H_2O}\left(\theta_{G,H_2O} - \theta_{L,H_2O}\right) - \frac{w(1-\varepsilon)}{\omega_G C^o_{G,H_2}}\left(\frac{-1}{4-\alpha} r_{H_2+CO} - r_{CO_2}\right) = 0 \tag{32c}$$

and the water-gas shift equation

$$\frac{\theta_{L,CO_2} \theta_{L,H_2}}{\theta_{L,CO} \theta_{L,H_2O}} - K_w = 0 \qquad (32d)$$

2.3 No mass transfer resistance in PMF model

The additional assumption is made that the reactants and products leaving the reactor in the liquid phase are negligible compared with those leaving in the gas phase. If the gas-liquid mass transfer resistance is assumed to be negligible, a mixed liquid phase now implies that the gas phase concentrations are constant.

If for each mole of CO and H_2 fed to the reactor t_1 moles of CO are converted via the F-T reaction and t_2 moles via the water-gas shift reaction, it follows that

$$U_G = U_G^o \left(1 - \frac{2}{4 - \alpha} X_{CO+H_2} \right) \qquad (33)$$

and

$$t_1 = \frac{X_{CO+H_2}}{4 - \alpha} \qquad (34)$$

Mole fractions of H_2, CO, H_2O and CO_2 are:

$$y_{H_2} = \frac{[I/(I + 1)] - \left((3 - \alpha)X_{CO+H_2} / (4 - \alpha) \right) + t_2}{1 - [2/(4 - \alpha)]X_{CO+H_2}} \qquad (35a)$$

$$y_{CO} = \frac{[1/(I + 1)] - X_{CO+H_2} / (4 - \alpha) - t_2}{1 - [2/(4 - \alpha)]X_{CO+H_2}} \qquad (35b)$$

$$y_{H_2O} = \frac{X_{CO+H_2}/(4 - \alpha) - t_2}{1 - [2/(4 - \alpha)]X_{CO+H_2}} \qquad (35c)$$

$$y_{CO_2} = \frac{t_2}{1 - [2/(4 - \alpha)]X_{CO+H_2}} \qquad (35d)$$

and

$$y_{C_n} = \frac{(1 - \alpha)^2 \alpha^{n-1} X_{CO+H_2} / (4 - \alpha)}{1 - [2/(4 - \alpha)]X_{CO+H_2}} \qquad (35e)$$