

CHAPTER 2

THEORITICAL

Chapter (2)

2-1- Solution of Selected Mathematical Model for Fischer-Tropsch Synthesis in Slurry Bubble Columns Reactor

A mathematical description for the simulation of the model of **Van der Laan et al. [1999]** Fischer-Tropsch SBCR is presented. The reactor model can be applied in the heterogeneous or churn-turbulent regime (see **Figure 2-1**). The large bubbles are assumed to be in plug flow with a superficial gas velocity of $U_G - U_{DF}$. The superficial velocity of the gas present in the mixed small bubbles is U_{DF} , which is equal to the total superficial velocity at regime transition. The mathematical model for the Fischer- Tropsch synthesis is based on the following assumptions:

- 1) Gas-liquid mass transfer resistance is located in the liquid phase.
- 2) Large gas bubbles are in plug flow due to high rise velocities, typically 1-2 m/s.
- 3) The gas phase in the small gas bubbles, and the liquid phase are each completely mixed, due to the large reactor diameter of 8 m.
- 4) Catalyst distribution is uniform due to up flow of the slurry phase, the large reactor diameter and the turbulence created by the fast-rising large bubbles.
- 5) Hydrocarbon products, paraffins and olefins only, in the gas and liquid phase of the reactor outlet are assumed to be in equilibrium.
- 6) The reactor operates isothermally due to the completely mixed liquid phase.
- 7) The slurry velocity is constant.
- 8) The reactor operates at steady state conditions.
- 9) The effectiveness factor of the catalyst particles is equal to unity and mass and heat transfer resistances between catalyst and liquid are negligible due to the small particle size applied ($50 \mu\text{m}$).

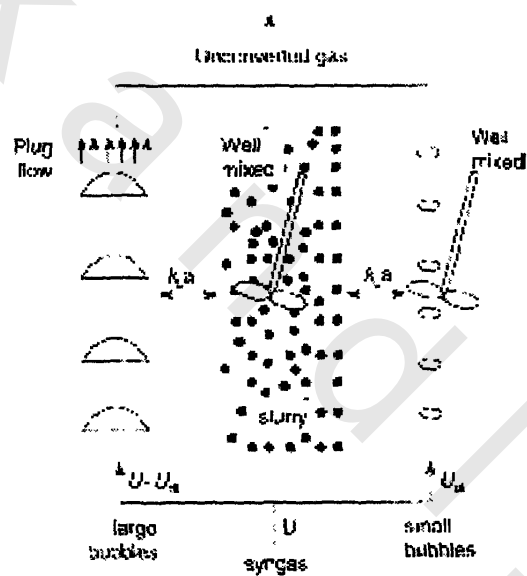
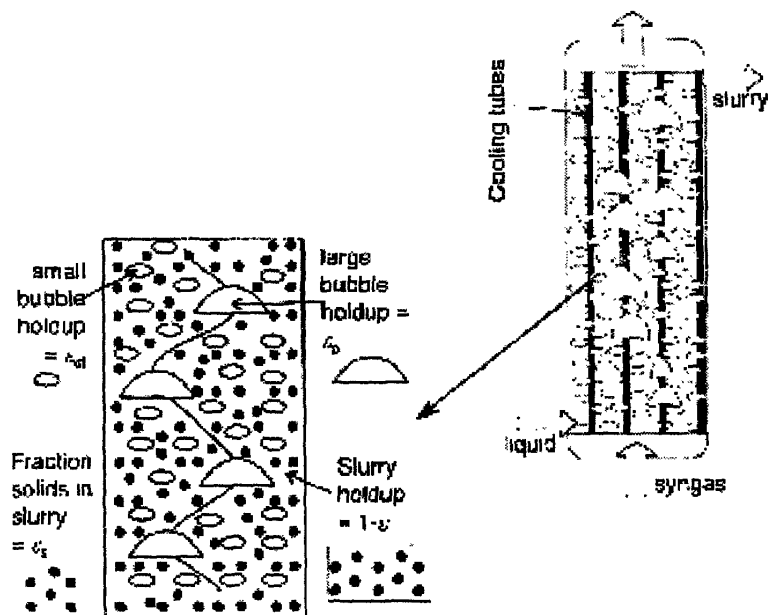


Figure 2-1. Conceptual Model of the Fischer-Tropsch Slurry Reactor

The balance equations for the two classes of bubbles of the gas phase and the liquid phase are the same as those given by **Shah et al. [1985]** and **Van der Laan et al. [1999]**. However, for the estimation of the hydrodynamic parameters the relations recommended by **Van der Laan et al. [1999]** are used in this work. This work is different from **Van der Laan's** work in the way of solution of the model equations which in the present case the model was solved analytically, that of **Van der Laan et al. [1999]** was solved numerically using a commercial software package. As was done by **Van der Laan et al. [1999]**, the α -Olefin Readsorption Product Distribution Model (ORPDM) of **Van der Laan et al. [1999]** was appended to the model to predict the hydrocarbon Product Distribution.

The gas phase mass balance for component i in large bubbles, rising in plug flow is:

$$\frac{1}{L} \frac{d(U_{LB})C_{i,G}^{large}}{dZ} + (k_L a)_i^{large} \left[\frac{C_{i,G}^{large}}{m_i''} - C_{i,L} \right] = 0 \quad (2-1)$$

With concentration in mol/m³ subject to boundary conditions at the reactor entrance $Z=0$:

$$C_{i,G}^{large} = C_{i,G0}$$

The gas phase mass balance for component i in the small bubbles (completely mixed) is

$$\frac{U_{DF}}{L} (C_{i,G0} - C_{i,G}^{small}) = (k_L a)_i^{small} \left[\frac{C_{i,G}^{small}}{m_i''} - C_{i,L} \right] \quad (2-2)$$

The mass balance for component i in the completely mixed liquid can be written as:

$$\int_0^1 (k_L a)_i^{large} \left(\frac{C_{i,G}^{large}}{m_i''} - C_{i,L} \right) dZ + (k_L a)_i^{small} \left(\frac{C_{i,G}^{small}}{m_i''} - C_{i,L} \right) + \varepsilon_L \varepsilon_P \rho_P \sum_{j=1}^n \nu_{ij} (R_j) - \left(\frac{U_S}{L} \right) C_{i,L} = 0 \quad (2-3)$$

The molar flow rate of the gas phase will change due to reaction. The superficial velocity is assumed to be a linear function of the overall synthesis gas conversion,

X_{CO+H_2} :

$$U_G = (1 + \alpha X_{CO+H_2}) U_{G0} \quad \text{or} \quad U_G = (1 + \alpha (1+U)/(1+F) X_{H_2}) U_{G0} \quad (2-4)$$

Where

α Contraction factor, defined as:

$$\alpha = \frac{U_G(X_{CO+H_2} = 1) - U_G(X_{CO+H_2} = 0)}{U_G(X_{CO+H_2} = 0)} \quad (2-5)$$

U is the usage ratio of hydrogen to carbon monoxide ($-R_{H_2}/-R_{CO}$) and F is the feed ratio of H_2 to CO . The reported values of α are between -0.5 and -0.65.

To calculate the cooling area requirements, the energy balance for the slurry phase, assuming the catalyst and the liquid temperatures to be equal is as follows [Van der Laan, 1999]:

$$\varepsilon_L \varepsilon_P \rho_P \sum_{j=1}^n (-\Delta H_{R,j} v_y(R_j) - h a_c (T - T_C)) + \left[\frac{U_s}{L} ((\rho_s C_{p,s} T)_m - (\rho_s C_{p,s} T)_{out}) \right] = 0 \quad (2-6)$$

where

The overall heat transfer coefficient, h is estimated from the correlation of **Deckwer et al. [1982]** as:

$$h = 0.1 U_G^{0.25} \rho_s^{0.75} C_{p,s}^{0.5} G^{0.25} \eta_s^{-0.25} \lambda_s^{0.5} \quad (2-7)$$

At gas velocities higher than 0.10 m/s the heat transfer coefficient does not increase any more and is calculated from equation (2-7) with U_G equal to 0.10 m/s

2-1- 1-Solution of the model equations

The variation in gas velocity is related to the conversion by the expression:

$$U_G = U_{G0} (1 + \alpha X_{H_2+CO}) \quad (2-8)$$

Where synthesis gas conversion is given by:

$$X_i = \frac{(U_{G0} y_{i,G0} - U_G y_{i,G})}{U_{G0} y_{i,G0}} \quad (2-9)$$

From equations (2-8) and (2-9)

$$U_G = \frac{U_{G0} (y_{i,G0} + \alpha y_{i,G})}{(y_{i,G0} + \alpha y_{i,G})} \quad (2-10)$$

Given that

$$C_{i,G} = \frac{y_{i,G} P}{R T} \quad (2-11)$$

Since the concentration of component i in the large bubbles vary along the length of the column, an average value of the driving force is used in the well-mixed liquid phase balance. Using the variation of gas velocity along the column, given by equation (2-10), a mass balance for reactant i in large bubbles is obtained.

$$-U_{LB0} y_{i,G0} (1 + \alpha) \frac{d}{dZ} \frac{y_{i,G}^{large}}{(y_{i,G0} + \alpha y_{i,G}^{large})} = \frac{(k_L a)_i^{large} R T L}{P} \left[\frac{P y_{i,G}^{large}}{m'_i} - C_{i,L} \right] \quad (2-12)$$

Thus equation (2-12) can be rewritten as:

$$\frac{-d y_{i,G}^{large}}{dZ} = \frac{(y_{i,G0} + \alpha y_{i,G}^{large})^2 (k_L a)_i^{large} R T L}{U_{LB0} (y_{i,G0})^2 (1 + \alpha) P} \left[\frac{P y_{i,G}^{large}}{m'_i} - C_{i,L} \right] \quad (2-13)$$

The boundary conditions for this equation is

$$\text{at } Z = 0 \quad y_{i,G}^{large} = y_{i,G0}$$

The liquid phase concentration of reactants is constant throughout the reactor and hence this equation can be integrated analytically as given in appendix A.:

Then finally this equation becomes:

$$Z = \frac{\bar{A}(y_{i,G}^{I\arg e} - y_{i,G0})}{(y_{i,G0} + \alpha y_{i,G}^{I\arg e})(y_{i,G0})(1 + \alpha)} + \frac{\bar{B}}{\alpha} \ln \frac{(y_{i,G0} + \alpha y_{i,G}^{I\arg e})}{(y_{i,G0})(1 + \alpha)}$$

$$+ \frac{\bar{C}}{b} \ln \frac{(a - b y_{i,G0})}{(a - b y_{i,G}^{I\arg e})} \quad (2-14)$$

Using the relation (2-11), the mass balance for the reactant i in the small bubbles equation (2-2) can be expressed as:

$$\frac{P}{RT} (U_{DF0} y_{i,G0} - U_{DF1} y_{i,G}^{small}) = L (k_L a)_i^{small} \left[\frac{P y_{i,G}^{small}}{m'_i} - C_{i,L} \right] \quad (2-15)$$

The mass balance for reactant i in small bubbles can be related to the liquid phase concentration as:

$$C_{i,L} = \frac{P y_{i,G0} U_{DF0}}{L R T (k_L a)_i^{small}} \left[\frac{y_{i,G0} - y_{i,G}^{small}}{y_{i,G0} + \alpha y_{i,G}^{small}} \right] + \left[\frac{P y_{i,G}^{small}}{m'_i} \right] \quad (2-16)$$

The mass balance for component i in the completely mixed liquid phase equation (2-3) can be written as:

$$(k_L a)_i^{I\arg e} \int_0^1 \left[\frac{P y_{i,G}^{I\arg e}}{m'_i} - C_{i,L} \right] dZ + (k_L a)_i^{small} \left[\frac{P y_{i,G}^{small}}{m'_i} - C_{i,L} \right]$$

$$+ \varepsilon_L \varepsilon_P \rho_P \sum_{j=1}^n \nu_y (R_j) - \left(\frac{U_s}{L} \right) C_{i,L} = 0 \quad (2-17)$$

From the liquid phase balance,

$$C_{i,L} = \left[\frac{(k_L a)_i^{small} \left[\frac{P y_{i,G}^{small}}{m'_i} \right] + (k_L a)_i^{I\arg e} \int_0^1 \frac{P y_{i,G}^{I\arg e}}{m'_i} dZ + \left[\varepsilon_L \varepsilon_P \rho_P \sum_{j=1}^n \nu_y (R_j) \right]}{(k_L a)_i^{small} + (k_L a)_i^{I\arg e} + \frac{U_s}{L}} \right] \quad (2-18)$$

The term $\int_0^1 \frac{P y_{i,G}^{large}}{m'_i} dZ$ can be evaluated by numerical methods e.g trapezoidal method.

Given the hydrodynamic and kinetic parameters estimated for specific reaction condition as given below, equations (2-14), (2-16) and (2-18) have to be solved simultaneously to obtain the value for $y_{i,G}^{small}$ and the profile for $y_{i,G}^{large}$. This is done by assuming a value for $C_{i,L}$ at a given Z level (say starting just above the bottom) of the slurry bubble column. Use equation (2-16) to solve for $y_{i,G}^{small}$ then equation (2-14) to solve for $y_{i,G}^{large}$. The procedure is repeated at other levels in the bed so as to scan the bed from Z=0 to Z=1. The integral term in the equation (2-18) is then calculated and $C_{i,L}$ is calculated from equation (2-18). If the calculated $C_{i,L}$ is equal to the assumed value within a certain allowable error then the assumed value is correct and so is all other values $y_{i,G}^{small}$ and the profile for $y_{i,G}^{large}$. If not then a new value for $C_{i,L}$ is estimated and so on.

In order to calculate the gas phase conversions for component i , the mass balance for the gas phase at the outlet of reactor can be written as:

$$U_{DF1} y_{i,G}^{small} + U_{LB1} y_{i,G1}^{large} = U_{G1} y_{i,G1} \quad (2-19)$$

or

$$\frac{U_{DF0} y_{i,G0} y_{i,G}^{small}}{(y_{i,G0} + \alpha y_{i,G}^{small})} + \frac{U_{LB0} y_{i,G0} y_{i,G1}^{large}}{(y_{i,G0} + \alpha y_{i,G1}^{large})} = \frac{U_{G0} y_{i,G0} y_{i,G1}}{y_{i,G0} + \alpha y_{i,G1}} \quad (2-20)$$

And

$$X_i = \frac{y_{i,G0} - y_{i,G1}}{y_{i,G1} + \alpha y_{i,G1}} \quad (2-21)$$

Thus, the overall conversion in the churn turbulent regime can be calculated if the fractional gas holdups, the rise velocities, and the volumetric mass transfer coefficients for two bubbles classes and kinetic data are known.

2-1-2- Hydrodynamics, Kinetics and Hydrocarbon Selectivity used in the model

2-1-2-1- Hydrodynamic parameters [Van der Laan et al., 1999]:

The most important hydrodynamic parameters are the gas holdups of the large and small bubbles in presence of solids under Fischer-Tropsch reaction conditions. The rise velocity of the small bubbles will increase with increasing solids holdup due to enhanced coalescence according to [Van der Laan, 1999]:

1-Gas holdup

For small bubbles,

$$V_{DF} = V_0 (1 + 0.8 \varepsilon_p / V_0) \quad (2-22)$$

$$\varepsilon_{DF} = \varepsilon_{D0} \left(\frac{\rho_G}{\rho_{G0}} \right)^{0.48} (1 - 0.7 \varepsilon_p / \varepsilon_{D0}) \quad (2-23)$$

Where $\varepsilon_{D0} = 0.27$: $V_0 = 0.095$ m/s, $\rho_{G0} = 1.3$ kg/m³

$$U_{DF0} = \varepsilon_{DF} V_{DF} \quad (2-24)$$

For large bubbles

$$U_{LB0} = U_{G0} - U_{DF0} \quad (2-25)$$

$$\varepsilon_{LB} = 0.3 U_{LB0}^{0.58} \left(\frac{\rho_G}{\rho_{G0}} \right)^{0.5} \quad (2-26)$$

The total gas holdup

$$\varepsilon_G = \varepsilon_{LB} + \varepsilon_{DF} (1 - \varepsilon_{LB}) \quad (2-27)$$

2- Mass transfer

The volumetric mass transfer coefficient of *large* bubbles is obtained from the relation proposed by Letzel et al. [1999]:

The $k_L a$ of small and large bubbles is obtained from the relation:-

$$k_L a_{small} = \varepsilon_{DF} (D_V / D_{V0})^{0.5} \quad (2-28)$$

$$k_L a_{large} = 0.5 \varepsilon_{LB} (D_V / D_{V0})^{0.5} \quad (2-29)$$

$$\text{Where } D_{V0} = 2 \times 10^{-9} \text{ m}^2/\text{s}$$

2-1-2-2- Kinetics and Hydrocarbon Selectivity

The rate expression for FT (iron or cobalt catalyst) as well as for water shift reaction (iron catalyst) on precipitated iron catalyst in the slurry phase proposed by [Maretto and Krishna, 1999] and [Van der Laan et al., 1999] was utilized.

a- For Cobalt catalyst (Maretto and Krishna, 1999)

$$R_{FT} = \frac{a_1 P_{CO} P_{H_2}}{(1 + b_1 P_{CO})^2} \quad (2-30)$$

where

$$a_1 = 8.8533 \times 10^{-3} \cdot \exp \left[4494.41 \left(\frac{1}{493.15} - \frac{1}{T} \right) \right] \quad (\text{mol}/(\text{s kg}_{\text{cat}} \text{ bar}^2))$$

$$b_1 = 2.226 \cdot \exp \left[-8236 \left(\frac{1}{493.15} - \frac{1}{T} \right) \right] \quad (1/\text{bar})$$

b - For Iron catalyst [van der Laan et al., 1999]

$$R_{FT} = \frac{k P_{CO} P_{H_2}^{0.5}}{(1 + a P_{CO} + b P_{CO_2})^2} \quad (2-31)$$

For water gas shift reaction iron only [Van der Laan et al., 1999].

$$R_{WGS} = \frac{K_{WGS} (P_{CO} P_{H_2O} - P_{CO_2} P_{H_2} / K_P)}{(P_{CO} + K P_{H_2O})^2} \quad (2-32)$$

c - The product selectivity

The product selectivity to α - olefins and paraffins was calculated using the selectivity model developed by [Van der Laan et al., 1999]. And given in chapter 1

equation (1-9) to equation (1-16) the appropriate model parameters determined experimentally by **Van der Laan et al., [1999]** are given in **table (2-1)**.

The optimization constraint for the selectivities

$$\sum_i^n m_i = 1$$

Henry constants for CO, CO₂, H₂, H₂O, N₂ were obtained from [**Marano and Holder, 1997**]. Diffusivities at high temperatures and pressures, necessary for calculating mass transfer coefficients were estimated using correlations of **Erkey et al., [1990]** utilized by **Van der Laan et al., [1999]**.

$$\text{The moles produced for component } i = \rho_p \varepsilon_L \varepsilon_p V_R R_{FT} m_i \quad (2-33)$$

A computer program has been developed to perform all the calculations. An overall executive program that calls servant subroutines at request for calculating physical properties, hydrodynamics parameters, reaction kinetics, selectivity, etc. and at the same time performs the main model calculations is constructed its algorithm is given in **figure (2-2)**. **Program listing is given in appendix B.**

Table (2-1) Kinetics and Hydrocarbon Selectivity model parameters at 523 K from [**Van der Laan et al., 1999**]

Parameter	Value	Parameter	Value
t_p^1	6.5	k (mol kg ⁻¹ s ⁻¹ MPa ^{-1.5})	0.0339
t_p^2	1.7	a (MPa ⁻¹)	1.185
k_R^2	(17.6) $k_R e^{2c}$	b (MPa ⁻¹)	0.656
C	0.35	K_{WGS} (mol kg ⁻¹ s ⁻¹)	0.0292
P	$14 P_{H_2}^{-0.26} P_{CO}^{0.40}$	K (-)	3.07
t_0	$3.71 P_{H_2}^{-0.5}$	K_p	85.81
k_R	$8*10^{-5} \frac{P_{H_2}^{1.2} P_{CO}^{-0.47}}{\phi_{V,0} / w}$		

Pressures in MPa, space velocity ϕ_{v0} / w in Nm³/kg_{cat} .s

Calculation Algorithm for Simulation of slurry bubble column reactor

1	Input physical properties of the gas, liquid and catalyst phases and reactor conditions - Calculation of Hydrodynamic Parameters
	a- Gas hold up (small and large bubbles) Input $V_0, \varepsilon_P, \rho_G, \rho_{G0}, \varepsilon_{D0}, P, T$ Apply equations (2-22 to 2-27) then Calculate $\varepsilon_{DF}, U_{DF}, U_{LB}, \varepsilon_{LB}, \varepsilon_G$
	b- Volumetric mass transfer coef.,1/s [Letzel et al. 1999]: For I =1 to NC (NC= H₂,CO,CO₂,N₂,H₂O) Input D_V, D_{V0} Apply equations (2-28, 2-29) then Calculate $k_{L,small}, k_{L,large}$ Next I
2	- Calculation of Physical Properties of slurry
	a- Slurry Density, ρ_{SL}, (kg/m³) apply equation (1-49) then Calculate ρ_{SL}
	b- Slurry Viscosity, μ_{SL}, (pa.s) apply equation (1-49) then Calculate μ_{SL}
	c- Slurry Heat Capacity, Cp_{SL}, (J/m³R) apply equation (1-49) then Calculate Cp_{SL}

	d- Slurry Thermal Conductivity; λ_{SL} ,(w/m.K) apply equation (1-31) then Calculate λ_{SL}
	e- slurry Heat transfer coeff., h Input $U_G, \rho_s, C_{p,s}, g, \eta, \lambda_s$ Apply equation(2-7) then Calculate h
3	Calculation of kinetic rate expressions
	a-For cobalt: [Maretto and Krishna 1999] Input a_1, b_1 Apply equations(2-30) then Calculate R_{FT}
	b-For iron (FT, WGS reaction) by Van der Laan et al. [1999] Input k, a, b, K_{WGS} , K, K_P Apply equations(2-31) then Calculate R_{FT}, R_{WGS}
4	For I =1 TO NC a-Assume $C_{i,L}$ <i>assumed</i> b-calculate $y_{i,G}^{small}$ from equation (2-16) at Z=0 $y_{i,G}^{large} = y_{i,G0}$ for Z=0 TO 0.999 calculate $y_{i,G}^{large}(Z)$ from equation (2-14) next Z c- perform the integration $\int \frac{P y_{i,G}^{large}(Z)}{m'_i} dZ$

	d-calculate the corresponding $C_{i,L} \text{ calc.}$ from equation f- if $\frac{C_{i,L} \text{ calc.} - C_{i,L} \text{ assumed}}{C_{i,L} \text{ calc.}} < 1 \cdot 10^{-4}$ then go to next step if not $C_{i,L} \text{ assumed} = C_{i,L} \text{ calc.}$ goto step b Next I
5	Calculation of the molar selectivity for hydrocarbons (C_1-C_{50}) by van der Laan et. al. [1999] Input t_p^1, t_p^2, c, k_R and Calculate p, t_0, k_R^2 Assume θ_i a- The molar selectivity for C_1 and C_2 by equations (1-14 to 1-16) c- The molar selectivity for carbon no >2 (olefins and paraffins) For I =3 to N Apply equations (1-11 to 1-13) Next I IF $\sum_1^N m_i = 1$ Then Calculate $\sum_1^N m_i$ Else assume another θ_i
6	For I =1 to N Apply equation (2-33) ($N = C_1 - C_{50}$) a- Calculate moles of component i (olefin and paraffin), moles/hr b- Calculate total outlet mass % of hydrocarbons products (olefin and Paraffin) c- Calculate total outlet mass of hydrocarbons products (olefin and paraffin contents), kg/hr Next I

Figure (2-2) Algorithm for the Model