1.0 INTRODUCTION

Coal can be converted into liquid fuels by direct or indirect liquefaction processes. The chemical composition of the liquid products from the two processes, however, are very different. The products of direct liquefaction are highly aromatic such as high octane gasoline and excellent feedstock for aromatic chemicals. On the other hand, the indirect liquefaction provides saturated hydrocarbon liquids such as high quality diesel fuel and intermediates for olefin production. Indirect liquefaction is considered as being more flexible than direct liquefaction as regards to the types of coal that can be used and the end products that can be produced.

Fischer-Tropsch synthesis represents an important route for indirect coal liquefaction. It is essentially hydrogenation of carbon monoxide which yield saturated and unsaturated compounds of the homologous series. It permits the synthesis of hydrocarbons ranging from methane to high melting paraffins depending on the catalyst, temperature and type of process employed. A small quantity of byproducts such as alcohols, aldehydes, ketones etc. are also formed. A variant of the FT synthesis is the production of methanol in high yields. Methanol is suitable for direct use as a turbine and transport fuel, although its energy content on a volume basis is only half that of gasoline (Derbyshire and Gray, 1985). It can also be used as a feedstock to produce high octane gasoline by employing the MOBIL Methanol-to-gasoline (MTG) process which uses a highly shape selective zeolite ZSM-5 catalysts (Kuo, 1982).

Several reactor configurations have been developed to produce liquid products by Fischer-Tropsch synthesis. The reactor systems used are: fixed bed reactor (ARGE), entrained bed reactor, fixed fluidized-bed reactor and slurry bubble column reactor. The fixed-bed reactor must operate with H_2/CO ratio in excess of unity, due to the possibility of plugging as a consequence of wax and/or carbon buildup (Kolbel and Ralek, 1980). The fluidized bed reactors are useful for producing gasoline, but cannot be operated under reaction conditions that lead to high molecular weight lubes and waxes due to agglomeration of catalyst particles. Three-phase slurry bubble column reactors provide an attractive alternative to the vapor-phase fixed and fluidized beds since they can be operated with low H_2/CO ratio (<0.6) synthesis gas in either a wax or gasoline producing mode. In addition these reactors also offer the advantages of high heat transfer rate, isothermal conditions of operation, reduced rate of catalyst deactivation due to washing effect of the liquid and on-line catalyst addition and withdrawal.

The objective of this project is to design and model a conceptual slurry reactor for two indirect liquefaction applications; 1) production of methanol and 2) production of hydrocarbon fuels via Fischer-Tropsch route. A slurry reactor is defined here as a three-phase bubble column reactor using a fine catalyst particle suspension in a high molecular weight liquid. The feed gas is introduced through spargers. It then bubbles through the column providing the agitation necessary for catalyst suspension and mass transfer. The reactor models for the two processes have been formulated using computer simulation. Process data, kinetic and thermodynamic data, heat and mass transfer data and hydrodynamic data have been used in the mathematical models to describe the slurry reactor for each of the two processes. Available data from process development units and demonstration units were used to test and validate the models. Commercial size slurry reactors for methanol and Fischer-Tropsch synthesis were sized using reactor models developed in this report.

2.0 Slurry Reactor Model:

The development of a reactor model starts with writing the differential mass and energy balance equations. The resulting differential equations can then be solved using suitable boundary conditions. The reactor design configuration, its operating conditions and process type also allow for some simplifying assumptions to be made. Since both methanol and FT synthesis reactors use fine catalyst particles suspended in liquid and operate at high pressures, some of the assumptions related to operating conditions are common to both reactor models. The kinetics and stoichiometry of the two processes are, however, very different. The products and stoichiometry of methanol synthesis process are well defined and leave the reactor in vapor phase. During FT synthesis, however, a large number of products are formed which makes it impractical to attempt individual component balance. For design purposes, however, some products can be grouped together without significant loss of accuracy. The following assumptions were made for the development of methanol synthesis and Fischer-Tropsch synthesis slurry reactor models.

2.1 Assumptions for Methanol Synthesis:

i) The total pressure within the reactor does not vary with axial position, i.e. the influence of hydrostatic head on gas expansion is neglected. This assumption is reasonable in view of the relatively high pressures used in the process.

ii) The effectiveness factors for the catalyst particles are taken as unity. Due to the relatively small particle sizes used in the reactors, diffusional limitations should be negligible.

iii) Again, as a consequence of the small particle size, mass and heat transfer resistances between the catalyst and liquid are assumed to be negligible.

iv) The gas and slurry phases are modeled using the axial dispersion model, the most appropriate model for bubble column reactors (Deckwer et al., 1983).

v) The catalyst is not uniformly distributed in the reactor and the sedimentation-dispersion model (Cova, 1966; Kato et al., 1972, Smith et.al, 1985) is used for modeling the catalyst concentration.

vi) The hydrodynamic parameters, namely gas holdup, interfacial area, heat and mass transfer coefficients and dispersion coefficients are assumed to be spatially independent.

vii) A heat balance will be made only on the slurry phase, since the heat capacity of the gas phase is much lower than that of the slurry.

viii) The temperature dependence of the total gas phase concentration $C_G=P/RT$ can be neglected since

$$d(1/T)/dz = -1/T^2(dT/dz) \sim 0$$

This approximation is justified since the temperature gradient is usually small due to liquid-phase back-mixing.

ix) Heat and mass dispersion in the slurry phase are equal and related by Lewis analogy, i.e.

$$D_L = (k_{eff}/ C_P)_L$$

x) Steady-state conditions prevail.

2.2 Assumptions for FT reactor model:

1) The synthesis products obey Schulz-Flory distribution. This assumption has been found to be valid over the entire range of products of an iron catalyst (Satterfield and Huff, 1982).

$$p_n=\alpha p_{n-1}=\alpha^{n-1}p_1 \tag{1}$$

Here, p_n refers to the product distribution as formed on the catalyst.

2) The hydrocarbon products consist of n-alkanes and n-alkenes only. These are in fact the main products of catalysts and little design error is introduced by lumping the methyl branched isomers with n-alkenes and n-alkanes.

3) The gas phase component balance is made only for i) CO, ii) H_2, iii) CO_2, iv) H_2O and v) C_1 to C_3 hydrocarbons. The contribution of hydrocarbons heavier than C_3 in the gas phase is estimated to be less than 4% of the gas flow rate in the reactor.

4) The effectiveness factors for the catalyst particles are taken as unity. Due to the relatively

small particle sizes (< 50 μm) used in the reactors, diffusional limitations should be negligible.

5) Again, as a consequence of the small particle size, mass and heat transfer resistances between the catalyst and liquid are assumed to be negligible.

6) The gas and slurry phases are modeled using the axial dispersion model, the most appropriate model for bubble column reactors (Deckwer et al., 1983).

7) The catalyst is not uniformly distributed in the reactor and the sedimentation-dispersion model (Cova, 1966; Kato et al., 1972, Smith et.al, 1985) is used for modeling the catalyst concentration.

8) The hydrodynamic parameters, namely gas holdup, interfacial area, heat and mass transfer coefficients and dispersion coefficients are assumed to be spatially independent.

9) The temperature dependence of the gas phase concentration $C_G = P/RT$ can be neglected since

$$d(1/T)dz = -1/T^2(dT/dz) \sim 0$$

10) Steady-state conditions prevail.

11) The vapor and liquid product streams leaving the reactor are in phase equilibrium.

2.3 Model Equations:

Based on the above assumptions, mass and energy balance were developed for the reactor model.

Gas Phase Mass Balance:

The gas phase mass balance with axial dispersion for component i can be written as:

$$\frac{1}{Pe_G}\frac{d^2y_i}{dz^2} - \frac{d(vy_i)}{dz} - (St_{G,i})(y_i - x_i) = 0 \qquad (2)$$

subject to the following boundary conditions:

$$vy_i - \frac{1}{Pe_G}\frac{dy_i}{dz} = y_{i,o} \qquad at\ z=0 \qquad (3)$$

$$\frac{dy_i}{dz} = 0 \qquad at\ z=1 \qquad (4)$$

The molar flow rate of gas will vary along the column due to reaction. The effect of change in molar flow rate on the superficial gas velocity can be determined by writing an overall mass balance. Thus

$$-\frac{dv}{dz} - \Sigma\, St_{G,i}(y_i - x_i) = 0 \qquad (5)$$

The above equation is subject to the boundary condition

$$v = 1 \qquad at\ z = 0 \qquad (6)$$

The volumetric flow rate of the gas will also vary along the column due to change in hydrostatic head. The local pressure along the column is given as

$$P(z) = P_T\,[1+h_o(1-z)] \tag{7}$$

where

$$h_o = \rho_{SL}g(1-\epsilon_g)L/P_T \tag{8}$$

Liquid Phase Mass Balance:

The liquid phase mass balance for component i can be written as:

$$\frac{1}{Pe_L}\frac{d^2x_i}{dz^2} - \frac{dx_i}{dz} + St_{L,i}(y_i-x_i) + \Sigma\theta_{i,k}(1-\epsilon_g)C_{cat}r_k(H_iL/PU_L) = 0 \tag{9}$$

subject to the following boundary conditions:

$$-\frac{1}{Pe_L}\frac{dx_i}{dz} + x_i = x_{i,o} \qquad at\ z=0 \tag{10}$$

$$dx_i/dz = 0 \qquad at\ z = 1 \tag{11}$$

Solid Phase Mass Balance:

The axial distribution of catalyst is governed by gravitational settling and axial dispersion due to agitation of the catalyst slurry by the gas flow. From assumption (8) the volume fraction of the liquid is constant along the column length and hence the mass balance on catalyst can be written as:

$$\frac{1}{Pe_s}\frac{d^2w}{dz^2} + \frac{dw}{dz} = 0 \tag{12}$$

with boundary conditions:

$$w - 1/Pe_s(dw/dz) = 0 \tag{13}$$

$$\int_0^1 w dz = 1 \tag{14}$$

An analytical solution to the above equation is possible and is given below:

$$w = \frac{Pe_s \exp(-Pe_s z)}{[1 - \exp(-Pe_s)]} \tag{15}$$

2.4 Determination of Model Parameters

An extensive literature search was undertaken to estimate various parameters in the above model equations. Justifications for selecting various correlations are summarized in the following paragraphs.

Gas Holdup

The gas holdup in slurry bubble columns is affected by a number of factors which include: physical properties and coalescing behavior of liquid, gas and liquid velocities, column diameter, gas distributor design, solids concentration, size and density. The gas holdup also depends on the operating flow regime in the column. The development of a general correlation which takes into account the effect of all these variables is indeed a difficult task. The work done by various researchers is summarized below:

There seems to be general agreement among researchers that the gas holdup and volumetric mass transfer coefficient decrease with increasing solids concentration for particle size larger than 10 micron (Kato et al., 1973; Kara et al., 1982; Koide et al., 1984). For particles smaller than 10 micron, the gas holdup can be higher than the solid free bubble column (Kara et al., 1982; Sada et al., 1986). The effect of suspended particles was generally found to diminish when the superficial gas velocity was higher than 0.1 m/s. Kato et al. (1973) found the gas holdups to decrease with increasing particle size over the size range used for their study (i.e. 60-175 micron). These results suggest that a correlation for gas holdup in slurry bubble columns should account for the effects of particle size as well as slurry concentration. While most of the literature work for hydrodynamic studies in slurry bubble columns has been carried out in aqueous solutions, Bukur et al. (1989) used Fischer-Tropsch waxes for their study. The data of Bukur et al. (1989,1990) is, therefore more relevant for our purposes. Experiments were conducted in both batch bubble column mode and continuous bubble column mode to investigate the effects of solids concentration (0 to 30 wt.%), solid particles type and size (iron oxide and silica particles; 0-5μm and 22-44μm). Two types of liquids, namely hydrotreated reactor wax (FT-300) and SASOL reactor wax were used. The operating conditions were generally selected to closely simulate slurry bubble column reactors for Fischer-Tropsch synthesis applications. It may be pointed out that Bukur et al. (1990) conducted their experiments at atmospheric pressure, using one gas only, therefore the effect of operating pressure (or gas density) was not studied.

Moreover, Bukur et al. (1990) data is limited to slurry concentration of upto 30 wt. %. The gas holdup data from PDU operation, however, indicate that for fine particle suspensions, the influence of slurry concentration becomes more significant at concentrations higher than 35 wt%.

Recent studies show that gas holdup in bubble columns generally increases with increasing operating pressure, hence gas density (Idogawa et al., 1987; Clark, 1990: Kojima et al., 1991). The influence of pressure has been found to depend on pressure level, distributor type, gas velocity and solids concentration. These results show that a correlation for gas holdup should account for the effect of operating pressure (or gas density). Most of the literature correlations, however, are based on data obtained at atmospheric pressure and usually for one gas, as a result these equations do not account for any influence of gas density. In solid-free bubble columns, a few gas holdup equations have been developed based on high pressure operation (Idogawa et al., 1985 and 1987) or experiments using various gases (Reilly et al., 1986; Hammer et al., 1984). There is, however, a lack of systematic research to investigate the influence of pressure on gas holdup in slurry bubble columns. The limited gas holdup values that have been reported in the literature for slurry bubble columns operating under high pressure are generally relatively high (Brown, 1984; Tarmy et al., 1984; Clark, 1990). The gas holdup data from Air Products and Chemicals PDU operation also demonstrates the influence of gas density on gas holdup. For similar operating conditions, higher gas holdups were obtained with CO-rich gases compared to H_2-rich gases.

Selection of Gas Holdup Correlation

Correlations for gas holdup in slurry bubble columns have been proposed by a number of researchers including Deckwer et al. (1980), Koide et al. (1984), Sada et al. (1986), Sauer and Hempel (1987) and Bukur et al. (1990). The hydrodynamics of solid-free bubble column have been investigated more extensively. Some of the well known correlations for solid-free bubble columns (i.e. Hughmark, 1967; Akita and Yoshida, 1973; Hikita et al., 1980) may prove useful for slurry bubble columns under certain operating conditions. Smith and Ruether (1985) modified the correlation of Hughmark (1967) for slurry bubble columns. It was observed that when liquid density was replaced by slurry density in the correlation of Hughmark (1967) the residual error was reduced for their slurry bubble column data. The modified correlation of Hughmark was, therefore, selected for further testing.

Relevant experimental data to test various literature correlations was available from Process Development Unit operation by Air Products and Chemicals for the development of slurry reactor technology for methanol synthesis. The experimental holdups for the PDU operation were obtained using the available information from different reports and the data provided by APCL engineers. Various literature correlations for the estimation of gas holdup (Table 1) were tested against this experimental gas holdup data. Table 2 gives average relative error, average absolute relative error and minimum and maximum errors for different correlations. It can be seen that correlations Hughmark (1967) and Hikita et al. (1980) predict gas holdup for the given system with average absolute error of 12% or less. Correlation of Hughmark (1967) can account for the effect of slurry concentration but does not account for the effect of gas density. While Hikita et al. (1980) correlation can account for the effect of gas density it fails to account for the effects of slurry concentration. In the slurry reactor model we decided to include correlations of Hughmark (1967) and Hikita et al. (1980). For a given run, either of these correlations can be selected for testing. Correlation of Hughmark (1967) is recommended for CO-rich gases and slurry concentration higher than 34 wt.% but lower than 38 wt%. Hikita et al. (1980) correlation is recommended for slurry concentrations below 35 wt.%.

All the literature correlations for gas holdup are based on a constant gas velocity along the column height. Gas velocity would, however, decrease significantly along the reactor height for both methanol synthesis and Fischer-Tropsch synthesis due to decrease in moles of products. The effect of decreasing gas velocity on gas holdup and other hydrodynamic parameters need to be investigated.

Table 1. Literature correlations for gas holdup

Hughmark (1967) as modified by Smith and Ruether (1985)

$$e_G = [2 + (0.35/U_G)(\rho_{SL}\sigma/72)^{1/3}]^{-1}$$

Akita and Yoshida (1973)

$$\frac{e_G}{(1-e_G)^4} = 0.2\left(\frac{gD_c^2\rho_L}{\sigma_L}\right)^{1/8}\left(\frac{gD_c}{\nu_L^2}\right)^{1/12}\frac{U_G}{(gD_c)^{0.5}}$$

Hikita et al. (1980)

$$e_G = 0.672\left(\frac{U_G\mu_L}{\sigma_L}\right)^{0.578}\left(\frac{\mu_L^4 g}{\rho_L\sigma_L^3}\right)^{-0.131}\left(\frac{\rho_G}{\rho_L}\right)^{0.062}\left(\frac{\mu_G}{\mu_L}\right)^{0.107}$$

Deckwer et al. (1980)

$$\epsilon_g = 0.053\, U_g^{1.1}$$

Koide et al. (1984)

$$\frac{e_G}{(1-e_G)^4} = \frac{0.227\left(\frac{U_G\mu_L}{\sigma_L}\right)^{.918}\left(\frac{g\mu_L^4}{\rho_L\sigma_L^3}\right)^{-.253}}{1+4.35\left(\frac{\epsilon_{s,sus}}{\rho_s}\right)^{.748}\left(\frac{\rho_s-\rho_L}{\rho_L}\right)^{.881}\left(\frac{D_cU_G\rho_L}{\mu_L}\right)^{-.168}}$$

Table 1. Cont'd

Sada et al. (1986)

$$\left[\frac{\epsilon_G}{(1-\epsilon_G)^3}\right]_{III} = 0.41\, U_t^{1/16}\, \epsilon_{s,sus}^{-(.125 U_t^{-0.18})} \left[\frac{\epsilon_G}{(1-\epsilon_G)^4}\right]_{II}$$

here

$$U_t = \frac{g(\rho_P - \rho_L) d_P^2}{18 \mu_L}$$

units of U_t and U_G are in cm

Sauer Hempel (1987)

$$\frac{\epsilon_G}{1-\epsilon_G} = 0.0277 [U_G/(\nu_{sus} g U_G)^{.25}]^{.844} [\nu_{sus}/\nu_{eff,rad}]^{-0.136} [C_{cat,avg}/C_{cat,b}]^{0.0392}$$

$$\nu_{sus} = \nu_L [1 + 2.5\epsilon_s + 10.05\epsilon_s^2 + 2.73x10^{-3} \exp(16.6\epsilon_s)]$$

$$\nu_{eff,rad} = 0.011 D_c [g D_c]^{0.5} [U_G^3/(\nu_{sus} g)]^{1/8}$$

Bukur et al. (1990)

$$\epsilon_G = 0.24 Fr_G^{0.28} Bo^{0.14}$$

Table 2. Comparison of various literature correlations

Correlation by	Avg. Abs. Relative Error (%)	Avg. Relative Error (Min & Max) (%)
Hughmark (1967)	12.	-4.0 (-18.0,38.)
Akita and Yoshida (1973)	34.	-34. (-45.,-8.7)
Hikita et al. (1980)	11.0	0.3 (-17.0,40.0)
Deckwer et al. (1980)	165.0	165.0 (28.0,286.0)
Koide et al. (1984)	36.0	-36.0 (-46.0, -8.4)
Sada et al. (1986)	16.0	-10.0 (-49.0,17.5)
Sauer and Hempel (1987)	17.5	-15.0 (-28.0,23.0)
Bukur et al. (1990)	20.0	-18.0 (-32.0,17.0)

Volumetric Mass Transfer Coefficient:

The estimation procedure for volumetric mass transfer coefficient in slurry bubble column reactors was analyzed critically in view of available correlations and mass transfer theory. Volumetric mass transfer coefficient in a slurry bubble column is affected by a number of variables which include gas velocity, diffusivity, physical properties of liquid, properties of solid particles, concentration of solids, coalescing behavior of the system and gas distributor. Volumetric mass transfer coefficient also depends on operating flow regime in the column i.e. bubbly flow, churn turbulent regime. Bubbly flow regime is characterized by bubbles of narrow size distribution, high gas holdup and mass transfer rate. Bubbly flow regime is obtained at low gas velocities (< 0.05 m/s) with fine gas distributors. As the gas velocity is increased, the flow regime moves to churn turbulent regime via an intermediate flow regime. In the churn turbulent regime ($U_G > 0.08$ m/s) the effect of gas distributor is negligible. Industrial slurry reactor are operated at high gas velocities (> 0.14 m/s) to achieve high throughput, therefore, these reactors operate in churn turbulent regime.

Several correlations are available in the literature for the estimation of volumetric mass transfer coefficient in slurry bubble columns (i.e. Koide et al., 1984; Nguyen-tien et al., 1985; Sauer and Hempel, 1987; Schumpe et al., 1987). There is no relevant data, however, to test the validity of these correlations for our purposes. The correlations of Koide et al. (1984) and Sauer and Hempel (1987) are based on limited set of data over narrow operating conditions. Although the correlation of Schumpe et al. (1987) is based on a large set of data, it requires the knowledge of fluid consistency index and flow behavior index for the slurry. This information may be difficult to obtain at reactor conditions. The correlation of Nguyen-tien et al. (1985) is based on a comprehensive study of gas-liquid mass transfer in three-phase contactors.

Nguyen-tien et al. (1985)

$$k_{La} = 0.39(1 - e_s/0.58)U_G^{0.67} \tag{16}$$

Nigam and Schumpe (1987) observed that for a batch operated slurry bubble column (no external recirculation of slurry) the mean solid fraction (e_s) should be replaced by solid fraction at the reactor bottom (e_{so}). Although, this correlation accounts for the effects of solids concentration and gas velocity, it is based on data obtained for oxygen mass transfer in aqueous solutions. For other systems, this correlation needs to be corrected for the effects of diffusivities, physical properties of liquid and coalescing behavior of the system.

<u>Correction for Diffusivity:</u>

Correlations for volumetric mass transfer coefficient in bubble columns (Akita and Yoshida, 1973; Ozturk et al.,1987) show that:

$$k_{La} \ \alpha \ D_l^{0.5} \tag{17}$$

This shows that, gas-liquid mass transfer in bubble column is governed by Higbie's penetration theory.

Correction for Physical Properties of Liquid and Slurry:

Volumetric mass transfer coefficient in bubble columns has been found to be affected by the viscosity, surface tension and density of the liquid medium (Akita and Yoshida, 1973; Hikita et al., 1981; Ozturk et al.,1987). Akita and Yoshida (1973) and Hikita et al. (1980) studied gas-liquid mass transfer in aqueous solutions, while Ozturk et al. (1987) used organic liquids for their study. The effects of changes in surface tension can be enhanced in aqueous solutions of oxygenated compounds (i.e alcohols) due to a simultaneous change in coalescing behavior of the liquid. The correlation of Ozturk et al.(1987) was, therefore, used to apply corrections for physical properties of liquid. It gives:

$$k_{La} \propto \sigma_L^{-.33} \mu_L^{-.08} \rho_L^{.37} \tag{18}$$

The correlation of Ozturk et al. (1987) is based on data obtained in solid-free bubble column. The surface tension effects are not expected to change due to presence of solids. The effect of slurry viscosity on mass transfer coefficient is accounted for by the term in brackets in the correlation of Nguyen-tien et al. (1985). For density correction in slurry bubble columns, the liquid density can be replaced by slurry density, since fine particles in slurry reactor form a homogeneous slurry phase. The correlation of Nguyen-tien et al. (1985) can, therefore, be corrected as below to estimate volumetric mass transfer coefficients in other systems;

$$(k_{La})_l = (k_{La})_W (D_l/D_{o,w})^{0.5} (\sigma_L/\sigma_W)^{-.33} (\mu_L/\mu_W)^{-.08} (\rho_{SL}/\rho_W)^{.37} \tag{19}$$

The above correlation is applicable to coalescing media, for noncoalescing media (and other high gas holdup conditions) it would give conservative estimates of volumetric mass transfer coefficient.

A number of correlations have also been proposed for volumetric mass transfer coefficient in solid-free bubble columns. These correlation generally do not account for the effects of solid particles on gas-liquid mass transfer rate. The correlation proposed by Akita and Yoshida (1973), however, includes a gas holdup term which would indirectly account for the effects of solids. The proposed correlation also accounts for physical properties of liquid and is based on a large set of experimental data. This correlation may overpredict the effect of reactor diameter for large diameter reactors (>0.15 m). Literature data, however, indicate little effect of column diameter on volumetric mass transfer coefficient for diameters larger than 0.15 m. Therefore, the effect of column diameter has been restricted to 0.15 m for this correlation. The modified correlation of Akita and Yoshida (1973) also has been included in the slurry reactor model and can be selected from the input data file.

Liquid Phase Dispersion Coefficient

While liquid phase dispersion in solid-free bubble columns has been investigated extensively, very little work has been done to measure liquid backmixing in slurry bubble columns.

However, in the suspension of fine catalyst particles used in Fischer-Tropsch synthesis reactors, there is expected to be little effect of the presence of solids on liquid mixing. The various correlations available in the literature for liquid phase dispersion in bubble column were compared by Wendt et al. (1984). The correlation proposed by Deckwer et al. (1974) provides a good estimate of the liquid phase dispersion coefficient. This correlation was, therefore, selected to predict liquid phase dispersion coefficient in slurry reactor.

Deckwer et al. (1974)

$$D_L = 0.68 D_C^{1.4} U_G^{0.3} \tag{20}$$

Gas Phase Dispersion Coefficient:

Only a few studies have investigated gas phase dispersion in bubble columns (Towell and Ackerman, 1972; Field and Davidson, 1980; Kawagoe et al., 1989). Kawagoe et al. (1989) observed that the correlation of Towell and Ackerman (1972) provided a good estimate of the overall gas phase dispersion coefficient in bubble columns. A recent report from Air Products and Chemicals (Topical Report: Tracer Studies in the LaPorte LPMEOH PDU, 1990), however, showed that literature correlations (Towell and Ackerman, 1972; Field and Davidson, 1980) over-predicted gas phase mixing by a factor of about three in their large diameter slurry bubble column reactor. A new correlation was then recommended based on the best fit of their data.

Towell and Ackerman (1972)

$$D_G=20.0D_C^2U_G \tag{21}$$

Air Products and Chemicals (1990)

$$D_G=21.7D_C^{1.5}U_G^{1.8} \tag{22}$$

Both the above correlations have been included in the slurry reactor model, however, correlation of Air Products and Chemicals (1990) is recommended for commercial size reactors.

Axial Solids Distribution:

Although several groups of researchers have investigated distribution of solids in slurry bubble columns, the work of Bukur et al. (1989), using Fischer-Tropsch waxes, is more relevant for our purposes. Bukur et al. (1989) observed that the axial distribution for the 0-5 μm and 20-44 μm iron oxide and silica particles were uniform for all runs in the continuous mode of operation. For batch mode of operation, the 0-5 μm particles showed only a slight gradient with high concentration towards the bottom of the column. However, with 20-44 μm particles significant gradients in axial solids distribution profiles were observed in the batch mode of operation. Bukur et al. (1989) also noted that the correlation of Smith and Ruether (1985) provided a good prediction of solids dispersion coefficient in slurry bubble columns.

Smith and Ruether (1985)

$$Pe_p=9.6(Fr_G^6/Re_G)^{0.114}+0.019Re_p^{1.1} \tag{23}$$

$$Re_p = Ar/18 \quad if\ Re_p < 0.05 \tag{24}$$

$$Re_p = (Ar/13.9)^{0.7} \quad if\ Re_p > 0.5 \tag{25}$$

Smith and Ruether (1985) have suggested the following equation for hindered settling velocity in particle swarm.

$$U_s = 1.1\, U_G^{0.026} U_t^{0.8} \epsilon_L^{3.5} \tag{26}$$

Physical, Thermodynamic and Transport Properties:

Various literature correlations and models were reviewed to select suitable methods for estimation of physical, thermodynamic and transport properties. Whenever possible, available experimental data were used to develop suitable correlations.

Properties of Liquid:

For its liquid phase methanol process development program, Air Product selected Drakeol 10 as the solvent. Drakeol 10 from Penreco was selected based on plant trials, when Witco announced discontinuation of Freezene-100. Drakeol 10 is 65% paraffinic and 35% naphthenic and with average carbon number of 25. The liquid phase in Fischer-Tropsch reactor was approximated by paraffinic liquid with average carbon number of 38. The equations for density, viscosity and specific heats for the liquid phase were developed as a function of temperature.

Diffusivities:

Akgerman measured the diffusion coefficients for synthesis gas in high molecular weight liquids (n-C_{20} and n-C_{28}) and FT waxes for a DOE contract DE-AC22-84PC 70032 at temperatures ranging from 373 to 534°K. The following correlation was proposed to estimate diffusion coefficients.

$$\frac{10^9 D_i}{T^{0.5}} = \frac{94.5(V_s - c_i V_{so})}{M_i^{0.239} M_s^{0.781} (\xi_i \xi_s)^{1.134}} \tag{27}$$

Here

$$c_l V_{so} = \frac{c_l N \xi_s^3}{\sqrt{2}} \tag{28}$$

$$c_l = 1.206 + 0.0632(\xi/\xi_s) \tag{29}$$

Henry Law Constants:

Chao and Lin (1987) investigated the solubilities of synthesis gas in high molecular weight solvents (n-C_{20}, n-C_{28} and n-C_{36}) and Fischer-Tropsch waxes for a DOE contract No. DE-AC22-84PC 70024. Solubilities of hydrogen, carbon monoxide, carbon dioxide, methane, ethane and ethylene were measured at temperatures in the range of 100-300°C and pressure 10-50 atm. Lee (1986) studied phase equilibria for syngas in Witco-40 and Freezene-100 oils. Graff et al. (1988) measured solubility of syngas in the temperature range of 210 to 260°C in another high molecular weight solvent (squalene). These authors observed that the Henry's coefficients could be well approximated by an equation of the form:

$$H_i = A_i \exp(B_i/T) \tag{30}$$

Following equations were obtained for Henry's constants from regression analysis of the data from Chao and Lin (C_{43} wax, temperature range 200 to 300°C).

$$H_{H2}=83.35\exp(604.7/T) \tag{31}$$

$$H_{CO}=151.0\exp(136.0/T) \tag{32}$$

$$H_{CO2}=297.0\exp(-582.4/T) \tag{33}$$

$$H_{CH4}=204.4\exp(-264.2/T) \tag{34}$$

$$H_{C2H6}=558.36\exp(-1118.87/T) \tag{35}$$

Kinetic Models for Methanol Synthesis:

In the synthesis of methanol, the following chemical reactions are primarily discussed:

$$CO+2H_2 \rightarrow CH_3OH \tag{36}$$

$$CO_2+H_2 \rightarrow CO+H_2O \tag{37}$$

$$CO_2+3H_2 \rightarrow CH_3OH+H_2O \tag{38}$$

Several researchers have investigated the kinetic rate for methanol synthesis, using $Cu/ZnO/Al_2O_3$ catalyst. The proposed models can be divided into power law rate expressions and mechanistic models.

Power law models for methanol synthesis in three-phase slurry reactors have been proposed by Berty et al. (1983), Wedel et al. (1988) and Lee(1990). The proposed models are shown below:

Berty et al. (1983)

$$r_{MeOH} = k_1\left(C_{H2} - \frac{C_{MeOH}}{K_{eq,1}C_{H2}C_{CO}}\right) \tag{39}$$

$$r_{WGS} = k_2\left(C_{H2} - \frac{C_{CO}C_{H2O}}{K_{eq,2}C_{CO2}}\right) \tag{40}$$

Here $K_{eq,1}$ and $K_{eq,2}$ are equilibrium constants for reactions 1 and 2 respectively. This model does not account for partial pressure of carbon dioxide.

Lee (1990)

$$r_{MeOH} = A\exp(-E/RT)(C_{H2} - C_{H2,eq}) \tag{41}$$

Here

$A = 3380\ \text{m}^3/\text{kg.s} \qquad E = 18{,}800\ \text{kcal/kmol}$

This model does not account for partial pressure of carbon monoxide and carbon dioxide.

Wedel et al. (1988) developed a power law rate expression based on a review of various literature models.

$$r_{MeOH} = 1.98x10^7\exp(-56343/RT)P_{H_2}^{0.4}P_{CO}^{0.18} - 2.15x10^{10}\exp(-85930/RT)P_{CH_3OH}^{0.13} \tag{42}$$

Since the power law rate expressions are empirical in nature, their applicability is limited to the narrow range of experimental conditions used for the study. Moreover, none of the proposed power law expressions account for the effect of CO_2 concentration on methanol production rate, while the results from Air Products and Chemicals clearly show the importance of CO_2

concentration on methanol production rate.

Graff et al. (1988) developed a mechanistic model for the kinetics of three-phase methanol synthesis based on extensive set of experiments. The proposed model is given below:

$$r_{MeOH,1}=\frac{k_{ps,1}K_{CO}(C_{CO}C_{H2}^{3/2}-C_{CH3OH}/(C_{H2}^{1/2}K_{c1}))}{1+K_{CO}C_{CO}+K_{CO2}C_{CO2})(C_{H2}^{1/2}+K_{H2O}/K_{H2}^{1/2})C_{H2O}} \qquad (43)$$

$$r_{WGS}=\frac{k_{ps,2}K_{CO2}(C_{CO2}C_{H2}-C_{H2O}C_{CO}/K_{c2})}{(1+K_{COC_{CO}}+K_{CO2}C_{CO2})(C_{H2}^{1/2}+(K_{H2O}/K_{H2}^{1/2})C_{H2O})} \qquad (44)$$

$$r_{MeOH,2}=\frac{k_{ps,3}K_{CO2}(C_{CO2}C_{H2}^{3/2}-C_{CH3OH}C_{H2O}/(C_{H2}^{3/2}K_{C3}))}{1+K_{CO}C_{CO}+K_{CO2}C_{CO2})(C_{H2}^{1/2}+(K_{H2O}/K_{H2}^{1/2})C_{H2O})} \qquad (45)$$

$$K_{C1}=1.7210^{-16}\exp(126011/RT) \qquad (46)$$

$$K_{C2}=5.81\,10\exp(-33760/RT) \qquad (47)$$

$$K_{C3}=K_{C1}K_{C2} \qquad (48)$$

The kinetic and adsorption constants are given in Graff et al. (1988).

The Graff et al. (1988) model is based on proper analysis of reaction mechanism for the reaction system. It also accounts for the effects of CO_2 concentration on methanol production rate. This kinetic model is, therefore expected to provide better predictions of the reaction rates over a wide range of operating conditions.

Stoichiometry of Fischer-Tropsch synthesis:

The products of Fischer-Tropsch synthesis range from methane to high molecular weight paraffins. FT synthesis products are known to obey Schulz-Flory distribution. The general stoichiometry of Fischer-Tropsch reaction can be given as:

$$\gamma_{CO}CO+\gamma_{H_2}H_2\rightarrow\gamma_{HC}C_nH_m+\gamma_{H_2O}H_2O \tag{49}$$

Water formed as primary product is converted to carbon dioxide by the water gas shift reaction in presence of iron catalyst.

$$H_2O+CO\rightarrow CO_2+H_2 \tag{50}$$

As shown by Stern et al. (1985), the stoichiometric coefficients (γ_i) and average number of carbon (n) and hydrogen (m) atoms in the hydrocarbon products can be expressed in terms of the probability of chain growth (α) and the fraction of paraffinic hydrocarbons (λ) variables.

$$\gamma_{CO}=\frac{1}{D} \tag{51}$$

$$\gamma_{H_2}=\frac{2+(1-\alpha)^2+\lambda\alpha(1-\alpha)}{D} \tag{52}$$

$$\gamma_{HC}=\frac{(1-\alpha)}{D} \tag{53}$$

$$\gamma_{H_2O}=\frac{1}{D} \tag{54}$$

$$D=3+(1-\alpha)^2+\lambda\alpha(1-\alpha) \tag{55}$$

$$n=(1-\alpha)^{-1} \tag{56}$$

$$m=2[(1-\alpha)^{-1}+(1-\alpha)+\lambda\alpha] \tag{57}$$

The value of chain growth probability factor (α) and fraction of paraffins in the product (λ) are a function of the catalyst and operating conditions. For the production of high molecular weight products, value of α has been found to be in the range of 0.85-0.95.

Two Chain Growth Probabilities in Fischer-Tropsch Synthesis:

There is also some evidence for two chain growth probabilities in Fischer-Tropsch synthesis (Huff et al., 1984; Bukur et al., 1989). Huff et al. (1984) observed a marked break on a Flory plot at carbon number of ten. At higher carbon numbers, hydrocarbons are produced with a much higher probability of chain growth than for lower carbon numbers. The carbon number distribution is interpreted in terms of a dual site mechanism that can be described by an extended Flory equation which accounts for the fraction of product formed on each type of site.

$$m_n = \beta(1-\alpha_1)\alpha_1^{n-1}+(1-\beta)(1-\alpha_2)\alpha_2^{n-1} \tag{58}$$

where m_n is the mole fraction of products containing n carbon atoms, β is the fraction of type I sites on the catalyst and α_1 and α_2 are the chain growth probabilities associated with the type I and type II sites respectively.

A more general approach for the stoichiometry of FT synthesis should account for the two chain growth probabilities. The values of γ_i, x and y are now expressed in terms of the following variables.

α_1, α_2	two chain growth probabilities
λ	the fraction of paraffinic hydrocarbons
β	fraction of type I sites on the catalyst

$$\gamma_{CO}=-\frac{\frac{\beta}{1-\alpha_1}+\frac{1-\beta}{1-\alpha_2}}{D} \tag{59}$$

$$\gamma_{H_2}=-\frac{2(\frac{\beta}{1-\alpha_1}+\frac{1-\beta}{1-\alpha_2})+\lambda[\beta\alpha_1+(1-\beta)\alpha_2]+[\beta(1-\alpha_1)+(1-\beta)(1-\alpha_2)]}{D} \tag{60}$$

$$\gamma_{H_2O}=\frac{\frac{\beta}{1-\alpha_1}+\frac{1-\beta}{1-\alpha_2}}{D} \tag{61}$$

$$D=3\left(\frac{\beta}{1-\alpha_1}+\frac{1-\beta}{1-\alpha_2}\right)+\lambda[\beta\alpha_1+(1-\beta)\alpha_2]+[\beta(1-\alpha_1)+(1-\beta)(1-\alpha_2)] \tag{62}$$

$$x=\frac{\beta}{1-\alpha_1}+\frac{1-\beta}{1-\alpha_2} \tag{63}$$

$$y=2\left[\left\{\frac{\beta}{1-\alpha_1}+\frac{1-\beta}{1-\alpha_2}\right\}+\lambda\{\beta\alpha_1+(1-\beta)\alpha_2\}+\{\beta(1-\alpha_1)+(1-\beta)(1-\alpha_2)\}\right] \tag{64}$$

Kinetics of Fischer-Tropsch Synthesis:

The reaction kinetics of Fischer-Tropsch synthesis over iron catalyst have been investigated by a number of researchers. The various kinetic expressions have been reviewed by Huff and Satterfield (1984) and Zimmerman and Bukur (1990). The rate expression proposed by Anderson (1956) was found to be particularly useful.

$$r_{FT}=\frac{k_\sigma P_{CO}P_{H_2}}{P_{CO}+a_1 P_{H_2O}} \tag{65}$$

This equation includes water inhibition effect. At synthesis gas conversion below about 60 % Equation (65) reduces to

$$r_{FT}=k_1P_{H_2} \tag{66}$$

Huff and Satterfield (1984) derived an alternate form of expression based on the observed hydrogen dependance for a fused-magnetite catalyst.

$$r_{FT}=\frac{k_2P_{CO}P_{H_2}^2}{P_{CO}P_{H_2}+b_1P_{H_2O}} \tag{67}$$

Equations (65) and (67) have the same form if the constant 'a$_1$' in Equation (65) depends on the H_2 partial pressure i.e. $a_1 = b_1/H_2$.

For precipitated iron catalyst (100Fe/0.3Cu/0.2K), Zimmerman and Bukur (1990) observed that Equation (65) gave a better fit to their data compared to Equation (67). Similar observations were made by Nettelhoff et al. (1985) using a precipitated, unpromoted iron catalyst. Based on these observations, kinetic expression given by Equation (65) was selected for precipitated iron catalyst in the FT reactor model. The rate constants and adsorption constants were obtained from experimental data of Zimmerman and Bukur (1990).

Water gas shift reaction:

The water gas shift reaction occurs readily over potassium promoted iron catalyst. The shift reaction enables CO rich feeds to be utilized efficiently without the need for external shift. Both

Equations (49) and (50) for the FT and WGS reaction must be considered to accurately predict both H_2 + CO conversions and H_2/CO usage ratio which requires knowledge of WGS kinetics. The following rate expression for water gas shift reaction has been selected based on literature information (Kuo, 1983; Zimmerman and Bukur, 1990).

$$r_{WGS}=k_{wo}\frac{(P_{CO}P_{H_2O}-P_{CO_2}P_{H_2}/K_P)}{P_{CO}+a_1P_{H_2O}} \tag{68}$$

It may be pointed out here that literature kinetic expressions for FT synthesis are based on partial pressures in the gas phase while in a slurry reactor the rate depends on the liquid phase concentrations.

Cobalt Catalyst:

Fischer-Tropsch synthesis on a cobalt catalyst has been investigated by a number of researchers (Sarup and Wojciechowski, 1988, 1989; Yates and Satterfield, 1991). Specific activity of cobalt catalyst is high for FT synthesis (Withers et al., 1990). The FT synthesis over cobalt catalysts produce mostly n-alkanes and 1-alkenes. However, in contrast to most iron-based FT catalysts, cobalt is not very active for the water gas shift reaction. Yates and Satterfield (1991) reviewed and tested various literature rate expressions for FT synthesis over cobalt catalyst. The following kinetic equation was recommended based on their study.