DESIGN OF SLURRY REACTOR
FOR INDIRECT LIQUEFACTION APPLICATIONS

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by

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OBJECTIVE

The objective of the program is to design and model a conceptual slurry reactor for two indirect liquefaction applications; production of methanol and production of hydrocarbon fuels via Fischer-Tropsch route.

TECHNICAL APPROACH

The slurry reactor model is formulated for computer simulation with suitable assumptions. Process data, kinetic and thermodynamic data, heat and mass transfer data and hydrodynamic data is used in the mathematical models to describe the slurry reactor for each of the two processes. The differential mass and energy balance equations are solved numerically using computer simulation. Experimental data from pilot plant and process development unit is used to test and validate the model.

Reactor Model

The development of mathematical model for a reactor starts with differential mass and energy balance equations. The resulting differential equations can be solved using suitable boundary conditions. The reactor design configuration and its operating conditions usually allow for some simplifying assumptions to be made. Slurry reactors can be operated in different modes, three commonly used configurations for slurry reactor are shown in Figure 1. In the external recirculation mode, a large part of reaction heat can be removed by an external heat exchanger.

When there is no external recirculation of slurry (Figure 1.3), all the heat of reaction is removed by an internal heat exchanger, which can significantly reduce the effective reactor volume. In the external recirculation mode with flashing (Figure 1.1), the slurry is pumped back to high reactor pressure from flash drum where dissolved products and reactants are removed from the slurry. The differential pressure across the pump is lower, when there is external recirculation without flashing (Figure 1.2).

The following assumptions made for the development of FT synthesis reactor model are generally applicable to slurry reactors with fine catalyst particles.

Model Assumptions:

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 both the processes.

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 phase is modeled using both the plug flow and the axial dispersion and slurry phase is modeled using the axial dispersion model.

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) Isothermal conditions prevail

x) Steady-state conditions prevail

Model Equations:

Based on the above assumptions, the following mass and energy balance were developed for the reactor model. Definitions of the variables, coefficients and dimensionless groups are given in the Notation.

Gas Phase Mass Balance:

The gas phase mass balance equations are same for both external recirculation and no external recirculation of slurry.

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

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

subject to the following boundary conditions:

$$vy_i - \frac{1}{Pe_G}\frac{dy_i}{dz} = y_{io} \qquad \text{at } z = 0$$

$$\frac{dy_i}{dz} = 0 \qquad \text{at } z = 1$$

The gas phase mass balance with plug flow for component i can be written as:

$$\frac{d(vy_i)}{dz} + (St_{G,i})(y_i - x_i) = 0$$

subject to the following boundary conditions:

$$vy_i = y_{io} \qquad \text{at } z = 0$$

The superficial gas velocity (U_G) will vary with the volumetric flowrate of gas along the column. The gas velocity can be determined by writing an overall mass balance: assumptions (i) and (viii) ensure negligible effect of change in pressure and temperature along the column. Thus

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

The above equation is subject to the boundary condition

$$v = 1 \qquad \text{at } z = 0$$

<u>Liquid Phase Mass Balance:</u>

The liquid phase mass balance for component i with external recirculation of slurry can be written as:

$$\frac{1}{(Pe_L)}\ \frac{d^2x_i}{dz^2} - \frac{dx_i}{dz} + St_{L,i}\ (y_i - x_i) + \Sigma\ \alpha_{i,k} e_l C_{cat} r_k (H_i L/PU_L) = 0$$

subject to the following boundary conditions:

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

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

The liquid phase mass balance for component i with no external recirculation of slurry can be written as:

$$\frac{d^2x_i}{dz^2} + \frac{k_{L,i}a\,L^2}{D_L\,e_l}(y_i - x_i) + \Sigma\alpha_{i,k}e_l C_{cat} r_k (H_i L^2/D_L P) = 0$$

Boundary conditions

$$\frac{dx_i}{dz} = 0 \qquad \text{at } z = 0$$

$$\frac{dx_i}{dz} = 0 \qquad \text{at } z = 1$$

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 (vi) the volume fraction of the liquid is constant along the column length and hence the mass balance on catalyst can be written as:

With external recirculation of slurry:

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

boundary conditions:

$$w - 1/Pe_s(dw/dz) = 0 \qquad \text{at } z = 0$$

$$wdz = 1$$

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

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

The solid phase mass balance with no external recirculation of slurry can be written as:

$$\frac{d^2w}{dz^2} + Pe_s' \frac{dw}{dz} = 0$$

with boundary conditions:

$$w = 0 \qquad z = \infty$$

$$wdz = 1$$

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

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

Estimation of Model Parameters:

Hydrodynamic Parameters

Hydrodynamic parameters for the reactor model were eastimated using appropriate correlations from literature. Justifications for the selection of suitable correlations are summarized below.

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 selection of gas holdup correlation(s) was based on a test of literature correlations, using the experimental data from Process Development Unit (PDU) reactor of Air Products and Chemicals. Table 1 gives average relative error, average absolute relative error and minimum and maximum errors for different correlations. It can be seen that three correlations (Hughmark, 1967; Hikita et al., 1980; Sauer and Hempel, 1987) give a reasonable prediction of gas holdups for the given system with an average absolute error of less than 15%. Correlation of Sauer and Hempel (1987) is based on data obtained in a slurry bubble column. It includes a slurry viscosity term to account for the effects of solid particles on gas holdups. The correlations of Hughmark (1967) and Hikita et al. (1980) are based on data obtained in solid-free bubble columns. Smith and Ruether (1985), however, observed that the correlation of Hughmark(1967) could predict the gas holdup in their slurry bubble column with an average error of about 7%, when the liquid density in the original correlation was replaced by the slurry density. The correlation of Hughmark for slurry bubble column was further modified slightly to reduce the average relative errors for the PDU data. The modified correlation of Hughmark, used in our reactor model is shown below:

$$e_G = [2 + (0.3/U_G)(\rho_{SL}\ \sigma/72)^{1/3}]^{-1}$$

This correlation was found to provide a better prediction of changes in gas holdup with changes in slurry concentration as compared to correlation of Sauer and Hempel (1987). Figure 2 shows a parity plot of measured and predicted gas holdups.

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

Table 1. Comparison of various literature correlations for gas holdups

Correlation by	Avg. Abs. Relative Error (%)	Avg. Relative Error (Min & Max) (%)
Koide et al. (1984)	34.4	34.4 (-47.0, -9.4)
Sada et al. (1986)	21.0	14.0 (-35.0,55.7)
Sauer and Hempel (1987)	12.0	-3.6 (-22.5,34.0)
Hughmark (1967)	11.3	-2.6 (-20.0,33.0)
Akita and Yoshida (1973)	31.6	-31.6 (-45.6,-7.2)
Deckwer et al. (1980)	190.0	190.0 (39.0,317.0)
Hikita et al. (1980)	10.4	0.5 (-22.3,32.6)

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, used to predict liquid phase dispersion coefficient.

Deckwer et al. (1974)

$$D_L = .68\,D_c^{1.4}\,U_G^{0.3}$$

Gas Phase Dispersion Coefficient

The correlation of Towell and Ackermann (1972) will be used to estimate the gas phase axial dispersion coefficient. In a recent study, Kawagoe et al. (1989) showed that the correlation of Towell and Ackerman (1972) gave a good estimate of the overall gas phase dispersion coefficient in bubble columns.

Towell and Ackerman (1972)

$$D_G = 20\,D_c^2 U_G$$

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 higher 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. The study of Bukur et al. (1989) also shows that the correlation of Smith and Ruether (19850 gives a good prediction of solids dispersion coefficient in slurry bubble columns.

Smith and Ruether (1985)

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

$$Re_p = Ar/18 \qquad \text{if } Re_p < 0.5$$

$$Re_p = (Ar/13.9)^{0.7} \qquad \text{if } Re_p > 0.5$$

where

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

and

$$Re_p = \frac{U_t d_p \rho_L}{\mu_L}$$

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

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

Volumetric Mass Transfer Coefficient:

Like gas holdup, volumetric mass transfer coefficient in slurry bubble columns has been found to depend on the concentration, density and size of solids used. The volumetric mass transfer coefficient was found to decrease with increasing solids concentration by most researchers. Correlations for volumetric mass transfer coefficient in slurry bubble columns have been proposed by Koide et al. (1984), Nguyen-tien et al. (1985) and Sauer and Hempel (1987). There is no relevant data available, however, to test the validity of these correlations for our purposes. The correlation of Nguyen-tien et al. (1985) is based on a comprehensive study of gas liquid mass transfer in three-phase contactors. Nigam and Schumpe (1987) verified the applicability of this correlation for batch operated slurry bubble columns (no external recirculation of slurry).

Nguyen-tien et al. (1985)

$$k_L a = 0.39\ (1 - \epsilon_{s,sus}/0.58) U_G^{0.67}$$

This correlation is based on data obtained for oxygen mass transfer in aqueous solutions. For other systems $k_L a$ can be corrected as below:

$$(k_L a)_i = (k_L a)_o (D_i/D_{o,w})^{0.5} (\mu_w/\mu_L)^{0.3}$$

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 was used to develop suitable correlations.

Properties of Liquid:

Two liquids namely, Freezene-100 and Drakeol 10 have been used by Air Products and Chemicals for its liquid phase methanol process development program. Drakeol 10 from Penreco was selected, based on plant trials, when Witco announced discontinuation of Freezene-100.

Following correlations were developed for density and viscosity of Drakeol 10.

Density:

Drakeol 10

$$\rho_L = 1038.8 - 0.635\ T \qquad \text{in kg/m}^3$$

Viscosity:

Drakeol 10

$$\mu_L = \exp(-12.415 + 2561.88/T) \qquad \text{in kg/m.s}$$

where T is in K

Specific Heat:

Following correlation was obtained for the specific heat of Drakeol 10.

$$C_{PL} = 0.668 + 0.0042\ T \qquad \text{in kJ/kg.K}$$

Properties of Suspension:

Suspension Density:

$$\rho_{sus} = V_{cat}\rho_{cat} + (1-V_{cat})\rho_L \qquad \text{kg/m}^3$$

where

$$V_{cat} = \frac{\rho_L W_{cat}}{\rho_{cat} - W_{cat}(\rho_{cat} - \rho_L)}$$

and

$$W_{cat} = M_{cat}/M_{sus}$$

Specific Heat:

Heat capacity of the slurry can be estimated, knowing the individual heat capacities of the liquid and solid.

$$C_{PS} = W_{Cat} {}^{*} C_{PC} + [(1-W_{Cat})^{*} C_{PL}]$$

Diffusivities:

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

$$\frac{10^9 D_i}{T^{0.5}} = \frac{94.5}{M_i^{0.239} M_s^{0.781} (\delta_i \delta_s)^{1.134}} (V_s - b_i V_{so})$$

Here $b_i V_{so} = b_i N \delta_s^3 / 2$

and $b_i = 1.206 + 0.0632 (\delta_i / \delta_s)$

Henry's Law Constants:

Chao and Lin 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 under DOE contract No. DE-AC22-84PC

70024. Solubilities of hydrogen, carbon monoxide, methane and ethylene were measured at temperatures in the range of 100-300°C and pressure 10-50 atm. Lee(1986) studied the phase equilibria for syngas in Witco-40 and Freezene-100 oils. Graff et al. (1988) measured solubility of CO, CO_2, H_2, CH_3OH and H_2O 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:

$$H_i = A_i \exp(B_i/T)$$

The solubility data for Freezene-100 was used to estimate the coefficients in above equation, since molecular weight of Freezene-100 is close to that of Drakeol 10.

Kinetic Models for Methanol Synthesis:

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

$$CO + 2H_2 = CH_3OH \qquad (1)$$

$$CO_2 + H_2 = CO + H_2O \qquad (2)$$

$$CO_2 + 3H_2 = CH_3OH + H_2O \qquad (3)$$

Several researchers have investigated the kinetic rate for methanol synthesis, using

$Cu/ZnO/Al_2O_3$ catalyst. The following kinetic models were selected for further testing in our slurry reactor model, since these kinetic models are based on data obtained in slurry phase reactors.

The proposed models can be divided into power law rate expressions and mechanistic models. Power law models for methanol synthesis have been proposed by Berty et al. (1983) and Wedel et al. (1988).

Berty et al. (1983)

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

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

Here $K_{eq,1}$ and $K_{eq,2}$ are equilibrium constants for reactions 1 and 2 respectively.

Reported values for rate constants:

$$k_1 = 3.914 \exp(-7489/T)$$

$$k_2 = 1.189 \times 10^{-2} \exp(-5068.4/T)$$

Wedel et al. (1988)

$$r_{MeOH} = 5.5 \exp(-13466/RT)\, p_{H2}^{0.4}\, p_{CO}^{0.18} - 5970 \exp(-20537/RT)\, p_{CH3OH}^{0.13}$$

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

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

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

$$r_{MeOH,3} = \frac{k_{ps,3}K_{CO2}(C_{CO2}C_{H2}^{3/2} - C_{CH3OH}C_{H2O}/(C_{H2}^{3/2}K_{c3}))}{(1 + K_{CO}C_{CO} + K_{CO2}C_{CO2})(C_{H2}^{1/2} + (K_{H2O}/K_{H2}^{1/2})C_{H2O})}(=r_{H2O,3})$$

$K_{c1} = 1.72\ 10^{-16}\ \exp(126011/RT)$

$K_{c2} = 5.81\ 10\ \exp(-33760/RT)$

$K_{c3} = K_{c1}K_{c2}$

The kinetic and the adsorption constants are described by

$k_{ps,1} = 1.66\ 10^{5}\ \exp(-93925/RT)$

$k_{ps,2} = 7.21\ 10^{17}\ \exp(-215130/RT)$

$k_{ps,3} = 8.52\ 10^{-1}\ \exp(-43425/RT)$

$K_{CO} = 9.01\ 10^{-12}\ \exp(92138/RT)$

$K_{CO2} = 3.15\ 10^{-5}\ \exp(34053/RT)$

$K_{H2O}/K_{H2}^{1/2} = 2.71\ 10^{-12}\ \exp(103030/RT)$

SIGNIFICANT ACCOMPLISHMENTS

Development of Computer Codes:

The model equations for the slurry reactor constitute a set of coupled second-order ordinary non-linear differential equations. These equations are not amenable to an analytical solution and therefore, a numerical method had to be used for solution. Orthogonal collocation techniques are particularly suitable for the solution of boundary value problems and the software package, COLSYS, developed by Ascher et al. (1981) was used for the numerical solution of the model equations. This method is based on spline collocation at Gaussian points using a B-spline basis. Approximate solutions are computed on a sequence of automatically selected meshes until a user-specified set of tolerances is satisfied.

Computer codes for the reactor model were developed with a modular approach to computer programming, to ensure easy modifications by the user. The codes were developed on a VAX 8700 computer at the University of Pittsburgh under a VMS operating system. Standard FORTRAN 77 was used for writing the codes since this will ensure transfer to other compatible systems.

Test of Reactor Model for Methanol Synthesis:

Effects of slurry recirculation patterns

The reactor model was used to predict the performance of the different types of reactor configurations shown in Figure 1. The performances of the reactors was measured by reactor productivity. Table 2 gives the productivities obtained for three types of reactors. External recirculation reactor with flashing gives highest productivity, followed by reactor with no external recirculation of slurry. External recirculation mode with flashing gives the lowest productivity.

Table 2. Effects of slurry recirculation patterns on reactor performance

Slurry Circulation Pattern	Productivity (mol/hr-kg)
External recirculation with flashing	23.5
External recirculation without flashing	21.8
No external recirculation of slurry	23.0

The predicted trends follow the expected performance. When the slurry is flashed at reactor outlet, the dissolved products and unconverted reactants are recovered. In addition, the recycle slurry reduces the concentration of dissolved products in the reactor, which can favorably affect an equilibrium controlled reaction. At Air Products and Chemicals, an increase in reactor productivity was observed when reactor configuration was switched from external recirculation without flashing to the mode with no external recirculation of slurry. Similar trends are also provided by our reactor model for the two types of reactor configurations (Table 2).

Comparison of Measured and Predicted Productivities for PDU Reactor:

The PDU reactor of Air Products and Chemicals for methanol synthesis was simulated using our reactor model. The kinetic expressions of Berty et al. (1983) and Wedel et al. (1988) were tested in the model. The reaction rate provided by Berty et al. model was much lower than by Wedel et al. model. The Wedel et al. (1988) model, however, is based on partial pressures in the gas phase and couldn't properly account for mass transfer effects in the model. For example, a decrease in volumetric mass transfer coefficient increased productivity slightly and vice versa. Although Berty's model properly accounts for mass transfer effects, it provides a lower reaction rate. Initial testing showed that Berty's model could not predict the performance of PDU reactor. The results indicated that this kinetic model is either based on low activity catalyst and/or large catalyst particles with effectiveness factor less than unity . The reaction rate predictions of Berty's model were improved based on the results of PDU reactor. For a selected run, the reaction rate constant was boosted until the predicted productivity and production rate matched the measured productivity and production rate. The modified rate constant was then used in the reactor model to predict the performance of PDU reactor for other runs (Ref. Table 4, Studer et al., 1989). Figure 3 is a parity plot of measured and predicted productivities for CO-rich feed gas. The predicted productivities are within 10% of the measured values for most of the runs. It can, however, be seen that the predicted values of productivities were low (by more than 20%) for runs with measured productivities above 28 mol/hr-kg. These high productivity were obtained at high space velocities (> 10 Nm^3/hr-kg) and gas velocities (> 0.155 m/s). As discussed below, the drop in predicted productivities could be attributed to the presence of dead zones or partially active zones (due to distributor effects) in the reactor.

The rate constant for Berty's kinetic model was increased, using the results of run E-8.1 for PDU reactor (Table 4, Studer et al.,1989). This run is based on high slurry concentrations (45.3 wt%) and low space velocity (6.7 Nm^3/hr-kg) which makes it a good candidate for the presence of dead zones. It is, therefore, likely that this run provided a lower reaction rate which was then used to predict the PDU reactor performance at other conditions. It was observed that the predicted productivities were low (by about 20%) for runs E-8.11 and E-8.13 (Table 4, Studer et al., 1989) when space and gas velocities were high. The high measured productivities for these runs could be attributed to significant reductions in dead zone volume due to better mixing around the distributor region. These results are being further investigated, using kinetic model of Graff et al. (1988).

Effects of Operating Variables

The reactor model was used to study the effects of space velocity and operating pressure on reactor productivity. Figure 4 and 5 show that the reactor productivity increased with increasing space velocity and operating pressure. These results follow the experimentally observed trends.

Parameter Sensitivity Analysis

Parameter sensitivity analysis was carried out for the following non-adjustable parameters.

- Liquid axial dispersion coefficient
- Volumetric mass transfer coefficient
- Gas holdup

Figure 6 shows that the reactor productivity decreased slowly with increasing axial dispersion coefficient. Doubling the axial dispersion coefficient decreased the productivity by less than 3%. This suggests that the reactor performance is less sensitive to liquid backmixing.

Figure 7 shows that the mass transfer may become important if the volumetric mass transfer coefficient falls below about 1.0 s^{-1} for hydrogen. The estimated values of volumetric mass transfer coefficient were generally less than 0.75 s^{-1}. However, reducing the mass transfer coefficient by half resulted in about 6% reduction in productivity. A similar reduction in kinetic rate constant reduced the productivity by about 40%. These results show that methanol synthesis in the slurry reactor is essentially kinetically controlled.

Figure 8 shows that production rate decreases with increasing gas holdup. The reactor productivity, however, did not change significantly. The production rate decreases due to decrease in catalyst concentration with increasing gas holdup.

CONCLUSIONS

Simulation of PDU reactor, using our reactor model, indicated presence of dead zone in slurry reactor at low space and gas velocities. These results are being further investigated. The final model will provide suitable warnings for the presence of dead zone or partially active zone in a slurry reactor.

NOTATIONS

a : gas-liquid interfacial area, m^{-1}

A : Arrhenius frequency factor (m^3/kg.s)

b_i :coefficient, a function of molecular sizes of solute and solvent

A_i,B_i :constants for component i in the equation for Henry's coefficient

C : liquid phase concentration (kmol/m^3)

C_{cat} : catalyst concentration, gm/cc slurry

$C_{cat,avg}$: average catalyst concentration, kg/m^3 slurry

$C_{cat,b}$: catalyst concentration at column bottom, kg/m^3 slurry

$C_{G,i}$: gas-phase concentration of component i, kmol/m^3

$C_{L,i}$: liquid-phase concentration of component i, kmol/m^3

C_G : total gas-phase concentration, kmol/m^3

C_{PC} : specific heat of catalyst particles (kJ/kg.K)

C_{PL} : specific heat of liquid (kJ/kg.K)

C_{PS} : specific heat of slurry (kJ/kg.K)

D_G : gas-phase dispersion coefficient, m^2/s

D_i : diffusivity of component i in the reactor liquid (m^2/s)

D_L : liquid-phase dispersion coefficient, m^2/s

$D_{o,w}$: diffusivity of oxygen in water (m^2/s)

D_S : solid-phase dispersion coefficient, m^2/s

H_i : Henery's constant for component i ($kmol/m^3.atm$)

H_o : static slurry height (m)

H_R : heat of reaction, kJ/kmol

$k_{L,i}$: liquid-side mass transfer coefficient for component i, m/s

k_La : volumetric mass transfer coefficient (s^{-1})

$(k_La)_i$: volumetric mass transfer coefficient for component i (s^{-1})

$(k_La)_o$: volumetric mass transfer coefficient for oxygen in aqueous phase (s^{-1})

$k_{ps,1}$ pseudo reaction rate constant for reaction 1 (kmol/kg.s.bar)

$k_{ps,2}$ pseudo reaction rate constant for reaction 2 (kmol/kg.s.bar)

$k_{ps,3}$ pseudo reaction rate constant for reaction 3 (kmol/kg.s.bar)

K adsorption equilibrium constant (1/bar)

K_p chemical equilibrium constant based on partial pressures

L : reactor length (m)

M_{cat} mass of catalyst in the suspension (kg)

M_{sus} total weight of the suspension (kg)

M_i molecular weight of diffusing component i (kg/kmol)

M_S molecular weight of solvent (kg/kmol)

N	Avogadro number
p_i	partial pressure of component i (MPa)
r	reaction rate based on weight of catalyst (kmol/kg.s)
r_k	: reaction rate for kth reaction, kmol/kg.s
R	: gas law constant (.082 m^3-atm/kmol.°K)
T	temperature (°K)
U_G	: gas superficial velocity, m/s
U_{Go}	: inlet gas superficial velocity, m/s
U_L	: liquid superficial velocity, m/s
U_s	: settling velocity of catalyst particles in swarm, m/s
v	: dimensionless gas-phase superficial velocity (U_G/U_{GO})
V_{cat}	volume fraction of catalyst in suspension
V_s	solvent molar volume (m^3/kmol)
V_{so}	the theoretical close-packed volume for solvent spheres of diameter o_s (10^{-6} m^3/mol)
w	: dimensionless catalyst concentration
W_{cat}	weight fraction of catalyst in suspension
x_i	: dimensionless liquid-phase concentration of component i ($C_{L,i}H_i/P$)
y_i	: mole fraction of component i in the gas phase
z	: dimensionless axial distance (x/L)

Dimensionless Numbers

Bo : Bodenstein number $(U_s H_o / D_s)$

Fr_G : Froude number for gas $U_G/(gD_c)^{.5}$

Pe_G : gas-phase Peclet number $(U_{Go} L / D_G \epsilon_G)$

Pe_H : Peclet number for heat transfer $(U_L L / E_L \epsilon_L)$

Pe_L : liquid-phase Peclet number $(U_L L / D_L \epsilon_L)$

Pe_S : solid-phase Peclet number $[(U_S - U_L/\epsilon_L)(L/D_S)$

Pe_S' : solid-phase Peclet number with no liquid flow $(\epsilon_L U_S L / D_S)$

Pe_p : particle Peclet number $(U_G D_c / D_s)$

Re_G : gas Reynolds number $(U_G D_c \rho_l / \mu_l)$

Re_p : particle Reynolds number $(U_t d_p \rho_l / \mu_l)$

St_G : gas-phase Stanton number $(K_{L,i} a L / U_{Go})(RT/H_i)$

$St_{L,i}$: liquid-phase Stanton number for component i $(K_{L,i} a L / U_L)$

Greek

α_{ik} : stoichiometric coefficient of component i in reaction k

ϵ_G : gas holdup

ϵ_L : liquid holdup

ϵ_s : solids holdup

$\epsilon_{s,sus}$: solids holdup in the slurry

μ_G : viscosity of gas phase (kg/m.s)

μ_L : viscosity of liquid phase (kg/m.s)

ρ_G : density of gas phase (kg/m^3)

ρ_L : density of the liquid phase, kg/m^3

ρ_{sus} : density of pseudo-homogeneous slurry (kg/m^3)

σ : surface tension of liquid (kg/s^2)

δ_i : molecular diameter of component i (A)

δ_s : molecular diameter of solvent (A)

Subscripts

CO : component CO

CO2 : component CO_2

CH3OH : component CH_3OH

H2O : component H_2O

G : gas phase

i : component i

k : kth reaction

L : liquid phase

o : inlet condition

S : solid phase

1 : methanol from CO reaction

2 : water gas shift reaction

3 : methanol from CO_2 reaction

ps : pseudo

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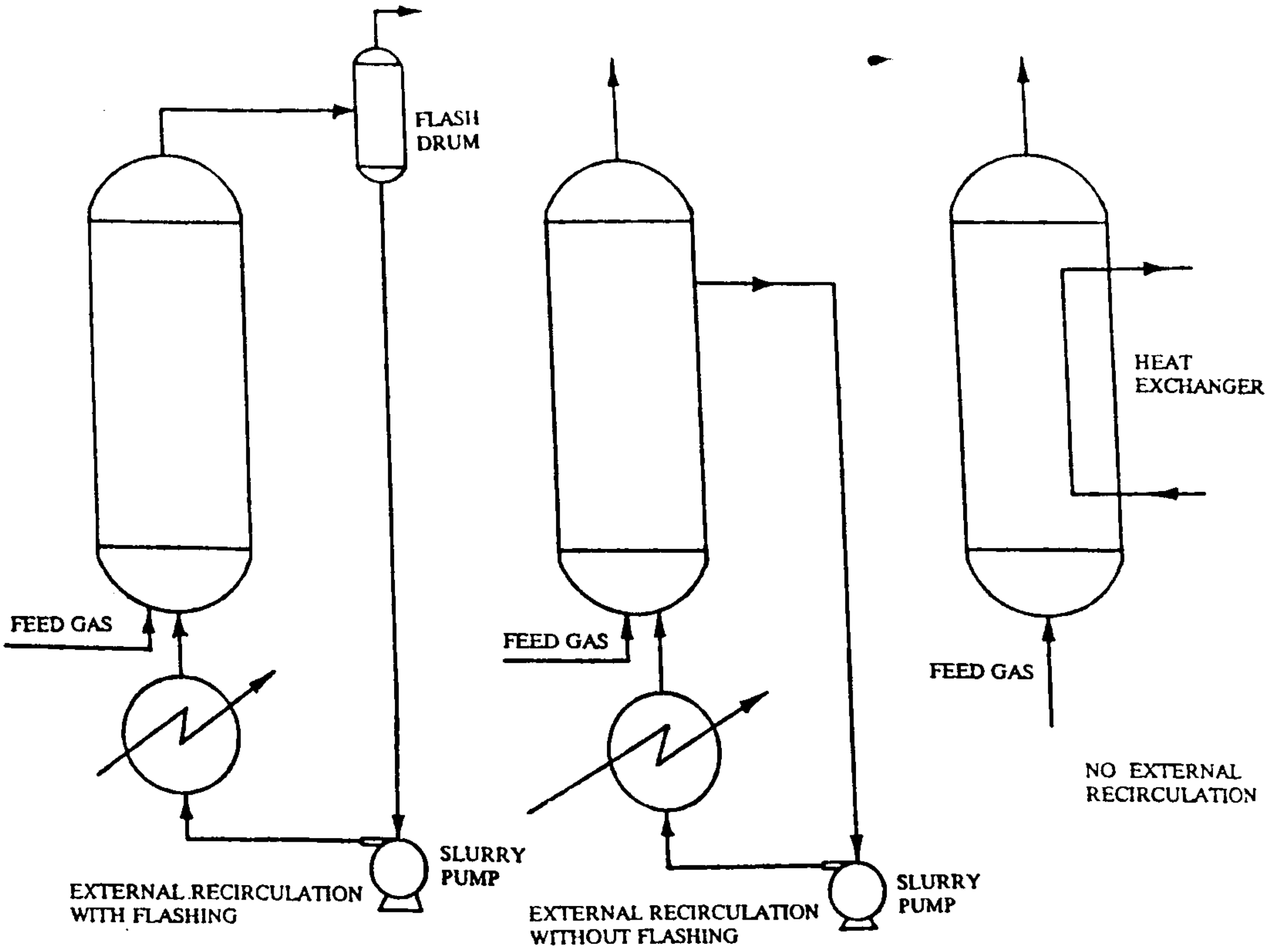

FIGURE 1.1

FIGURE 1.2

FIGURE 1.3

Figure 1. Different types of slurry reactor configurations

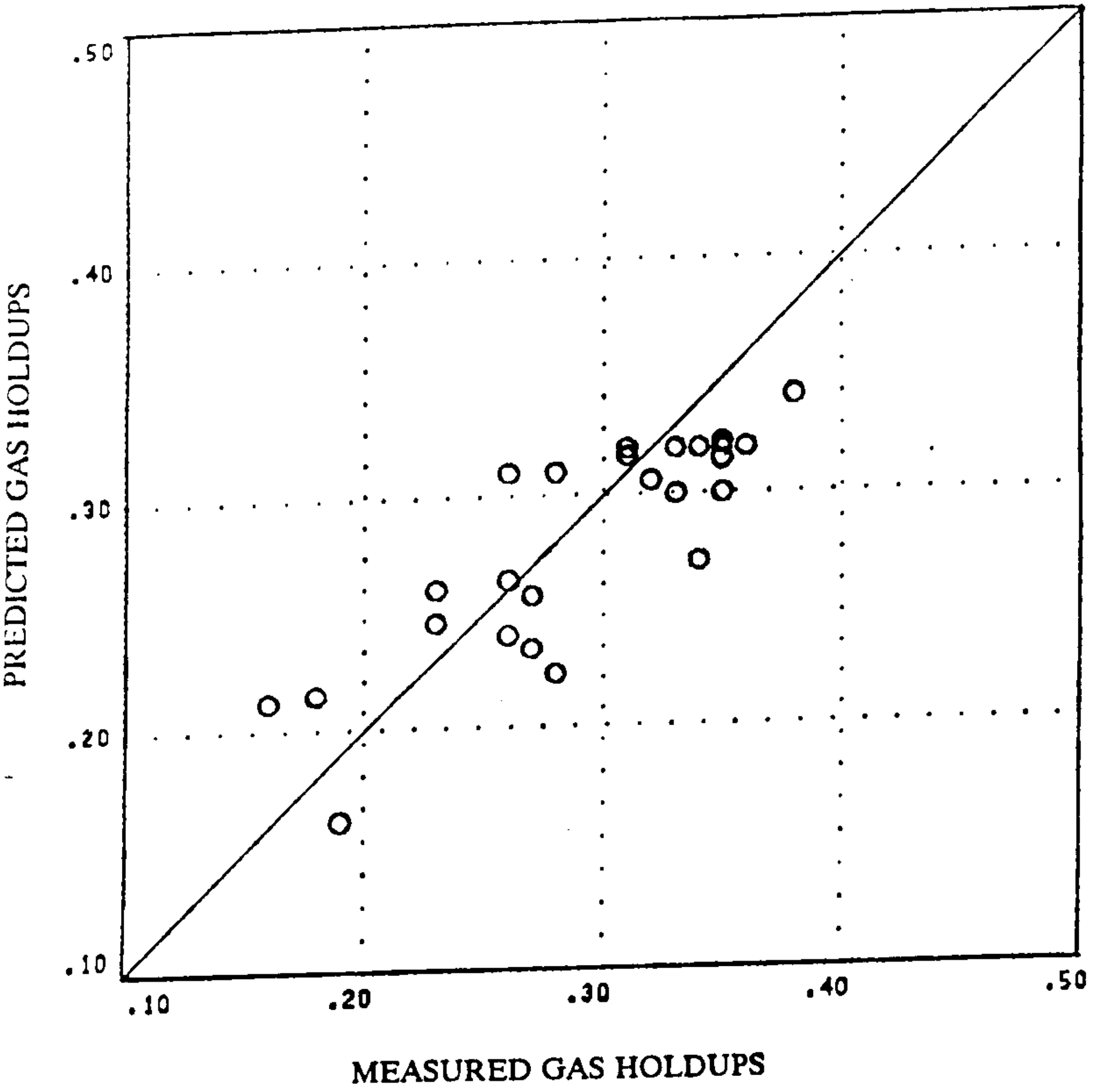

Figure 2. Parity plot of measured and predicted gas holdups

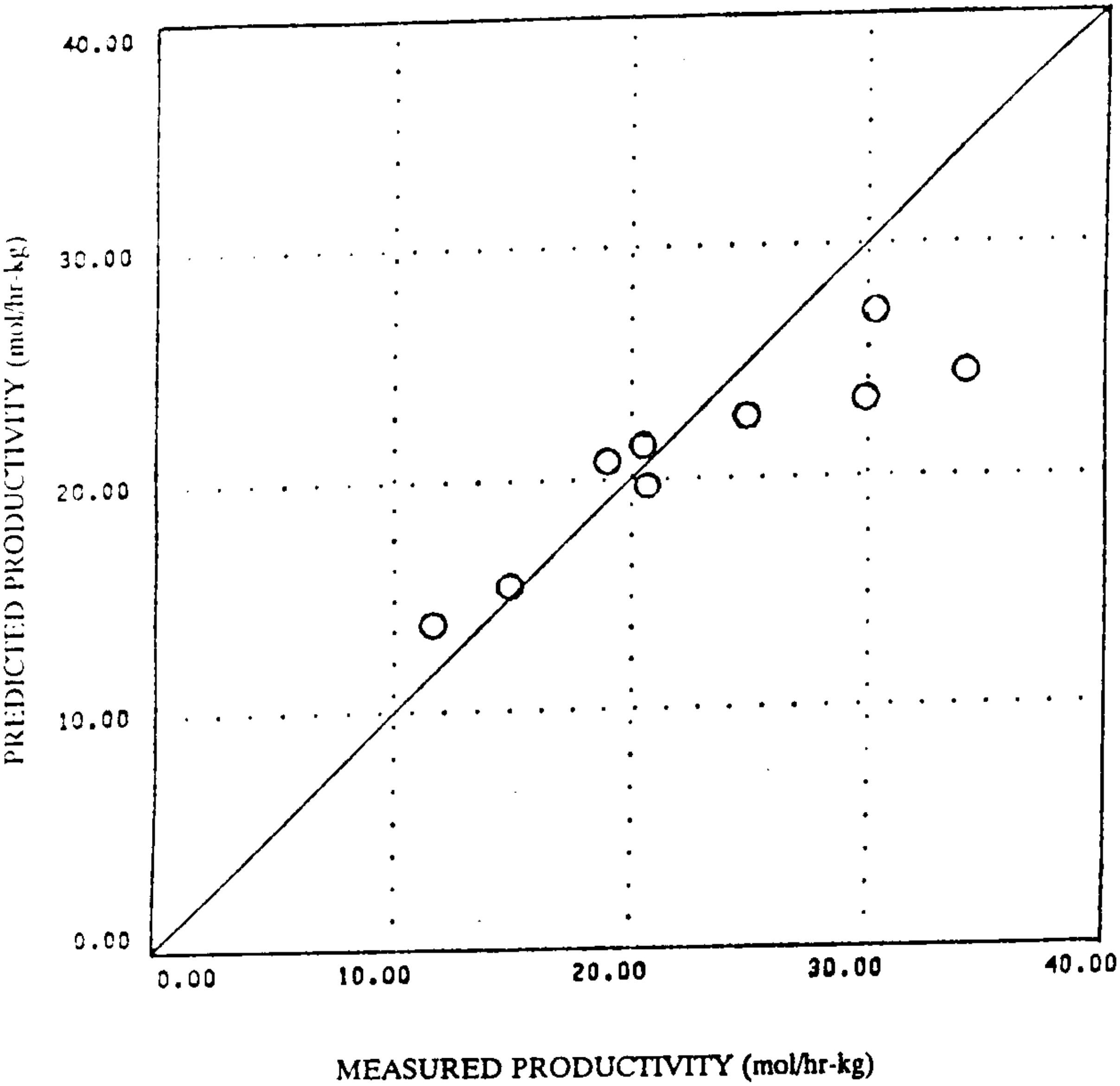

Figure 3. Parity plot of measured and predicted productivity

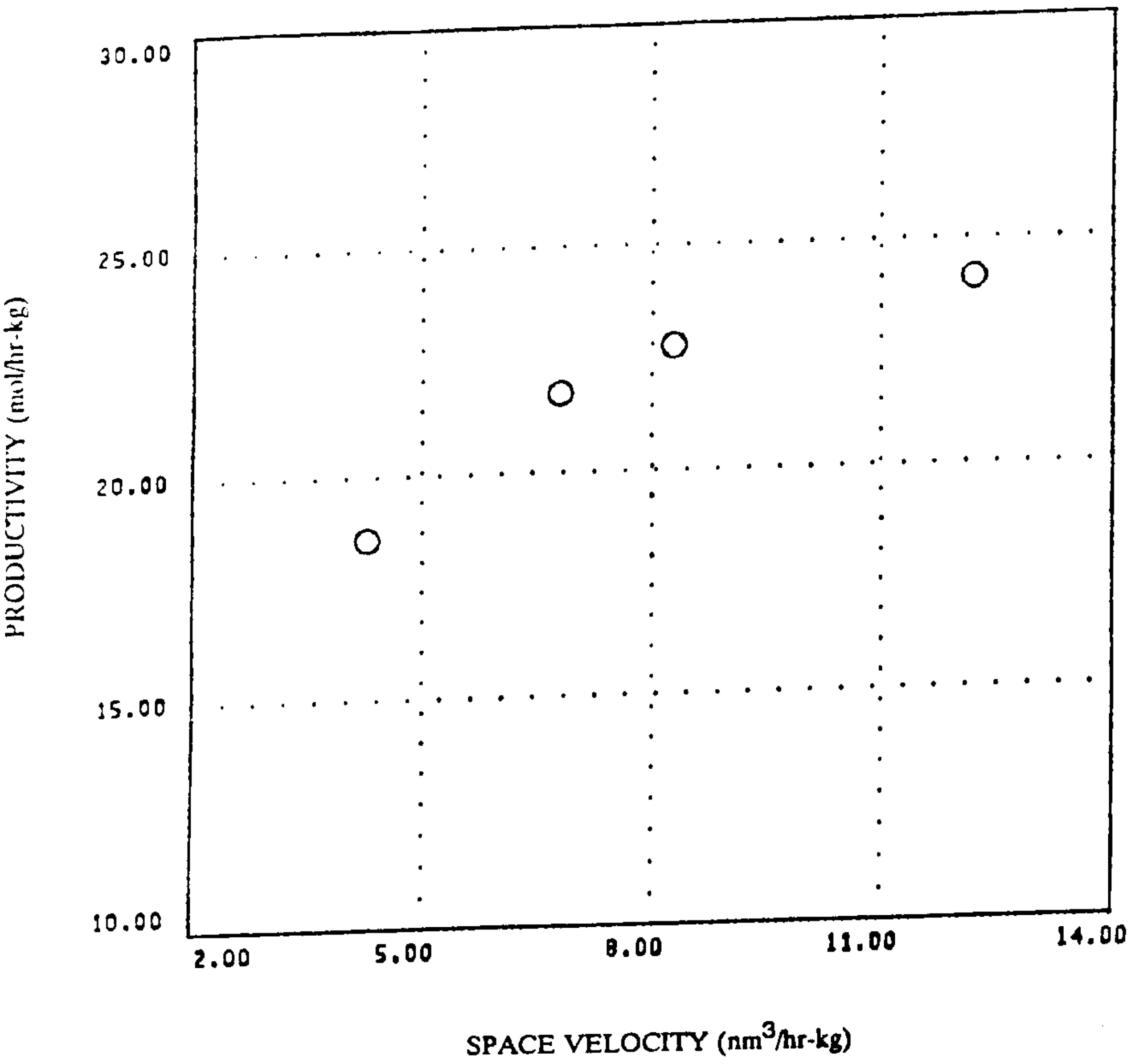

Figure 4. Effect of space velocity on productivity

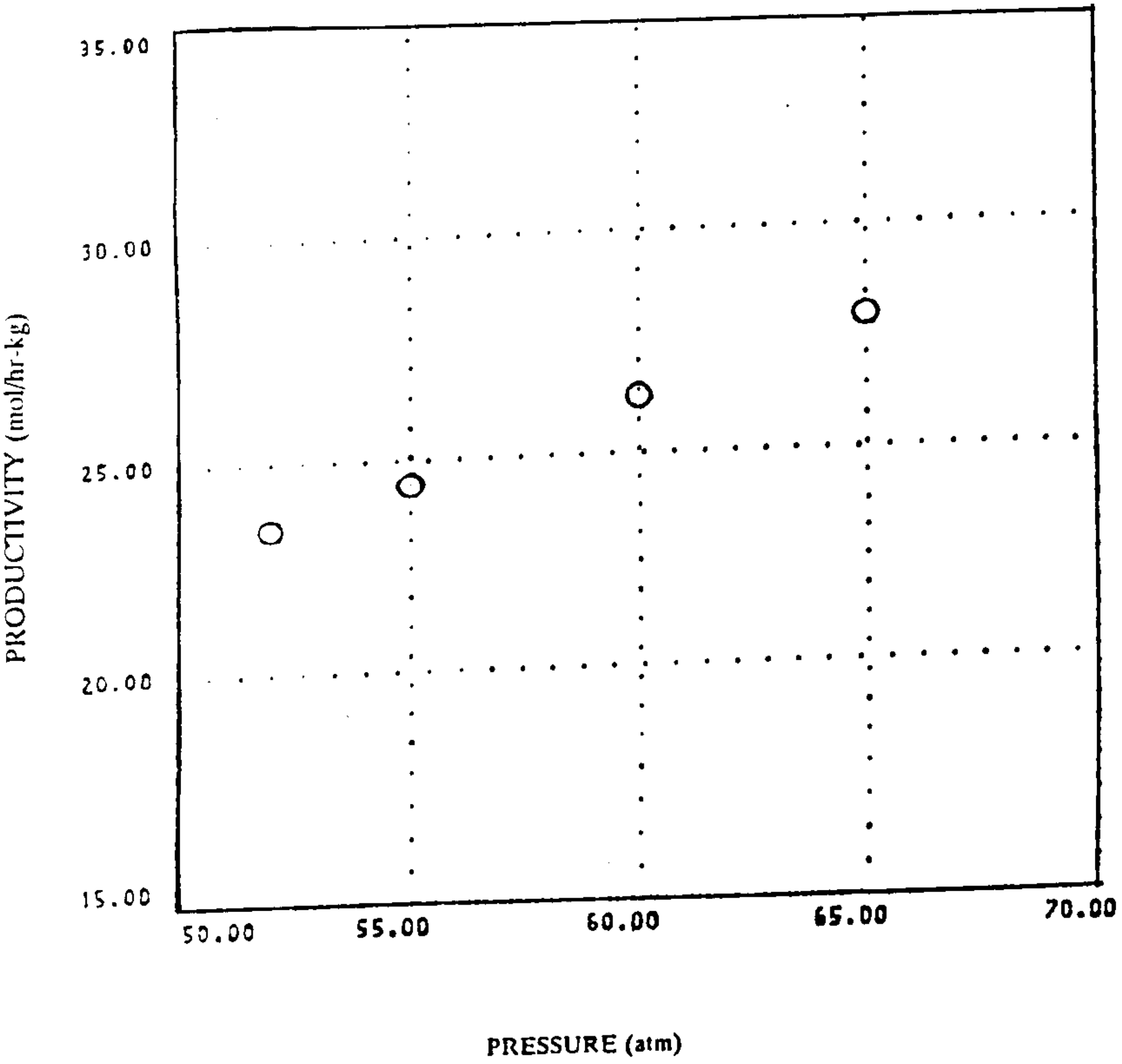

Figure 5. Effect of operating pressure on productivity

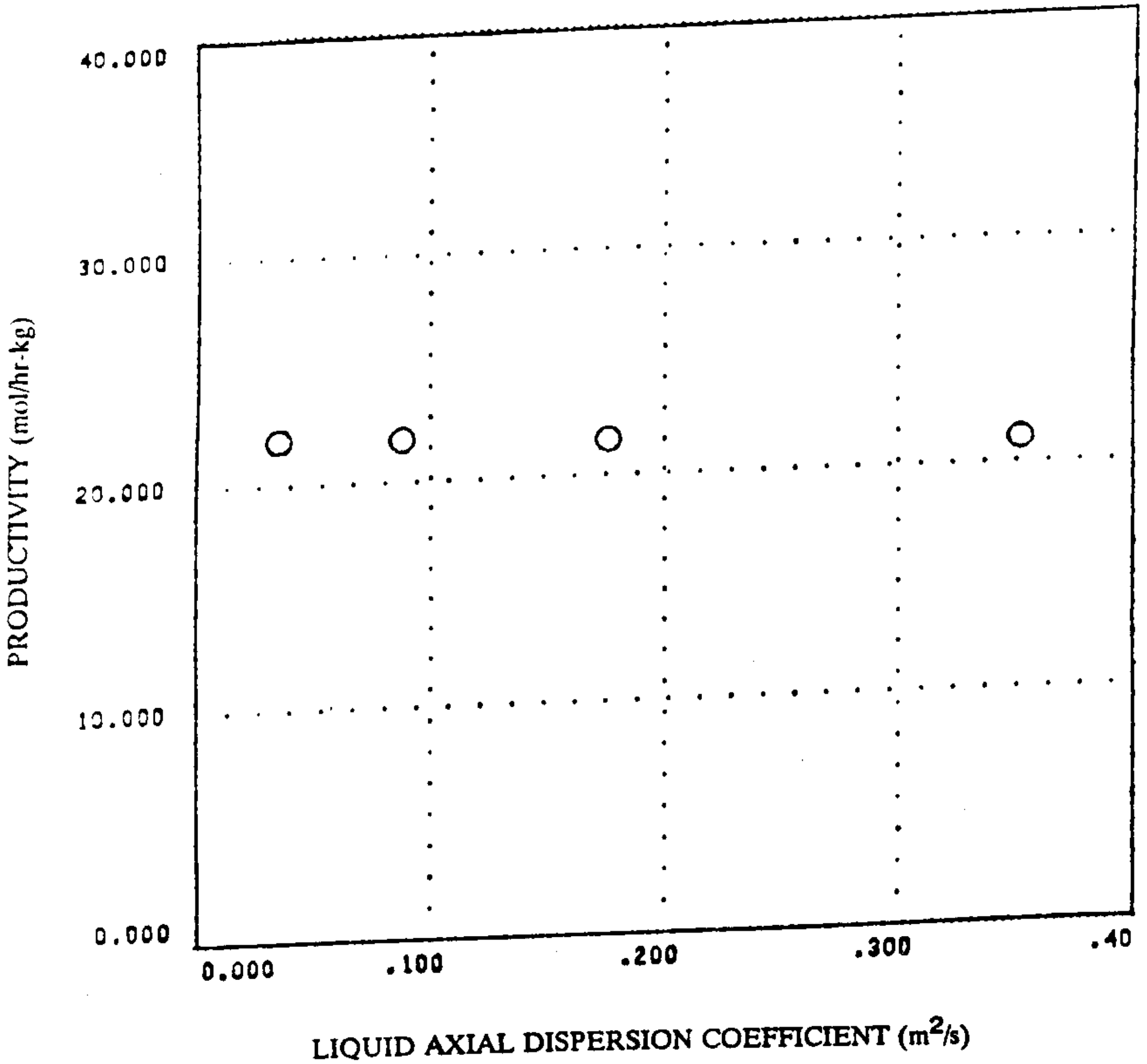

Figure 6. Effect of liquid axial dispersion coefficient on productivity

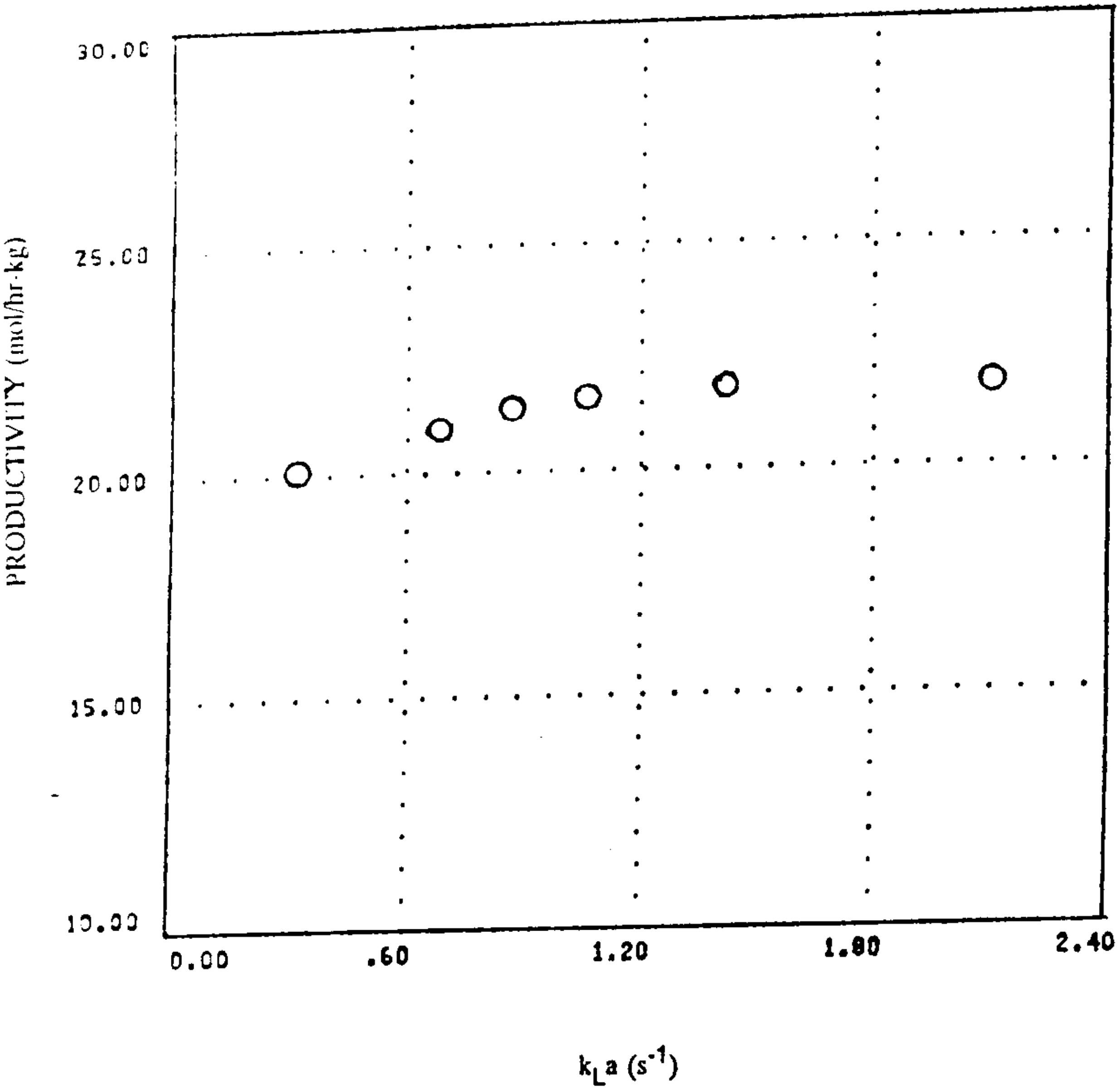

Figure 7. Effect of volumetric mass transfer coefficient on productivity

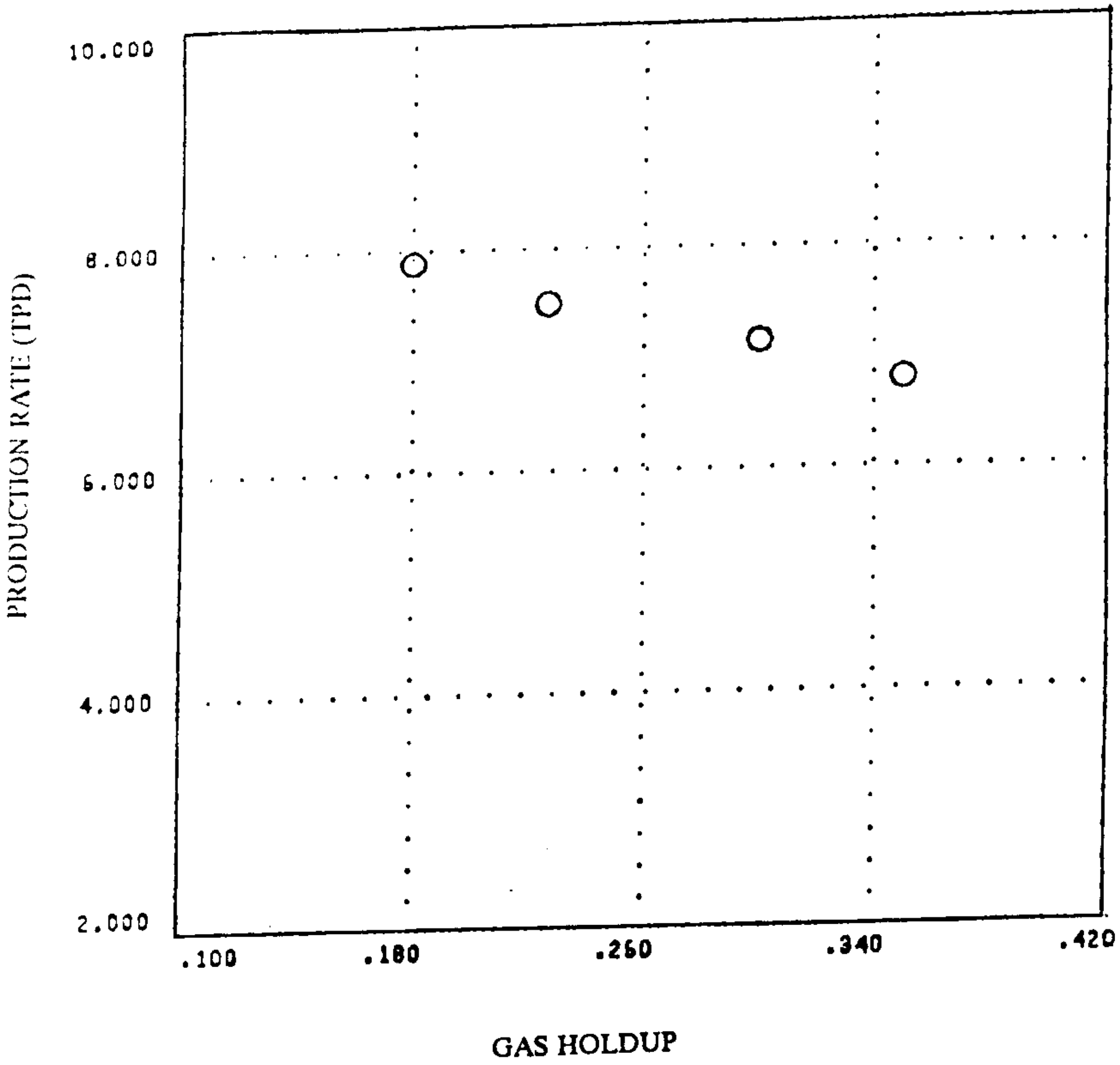

Figure 8. Effect of gas holdup on production rate