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Mass Transfer Studies in Multiphase System – A Review

D. Moghekar^a, H. M. Jena^a, G. K. Roy^a, B. C. Meikap^b

^aDepartment of Chemical Engineering, NIT, Rourkela-769008

^bDepartment of Chemical Engineering, IIT, Kharagpur-721302

Abstract:

Three phase systems are vital part of chemical industry, as reactions involving gas, liquid, and solid are often encountered in chemical process industry, of these, reactions in hydroprocessing industry, catalytic oxidation and hydration reactions are most common. The performance of such systems is controlled by the transport of mass between various phases. For the successful design and operation of especially three-phase system, requires through knowledge of interphase mass transfer. Indeed, the mass transfer depends on interfacial area and mass transfer coefficient. Many researchers have carried out study of such phenomena since last thirty years. Different methods have been used for the determination of interfacial area and mass transfer coefficient. Use of fiber optic probe is encouraged due to its accurate measurement of interfacial area. The interfacial area is found to be a strong function of gas superficial velocity. Physical and chemical methods were adopted for the determination of mass transfer coefficient. Chemical methods were much followed as it dose not require knowledge of flow regimes and accurate analytical method. Simultaneous measurement of interfacial area and mass transfer coefficient is beneficial as it give values of these at same hydrodynamic and physico-chemical conditions. The mass transfer coefficient increases with gas superficial velocity but a weak function of liquid superficial velocity. The mass transfer in phenol degradation increases with Reynolds number and phenol feed concentration.

1. Introduction

Three phase systems are vital part of chemical industry, as reactions involving gas, liquid, and solid are often encountered in chemical process industry. The most common occurrence of this type of three phase systems is in hydroprocessing industry, in which a variety of reactions between hydrogen, an oil phase, and solid catalyst have been found. The other common three phase catalytic reactions are oxidation and hydration reactions. The three-phase reaction system is subcategorized as

- Reactions where the gas, liquid, and solid are either reactants or products.
- Gas-liquid reaction with solid as a catalyst.
- Two reaction phases and third as inert phase

Various reactors like fixed bed, agitated vessels, bubble column, fluidized bed and semi-fluidized bed reactors are implemented to carry out reactions in three phase systems. The successful design and operation of gas-liquid-solid systems depends on the ability to accurately predict the fundamental characteristics of the system. Specially, the hydrodynamics, the mixing of individual phases, and the heat and mass transfer characteristics. Especially for multiphase reaction systems the knowledge of mass transfer and interfacial mass transfer area is vital for reactor design. The importance of gas-liquid, liquid-solid mass transfer on reactor performance depends upon the nature of reaction system and the flow conditions in the reactor [1]. The two important parameters characterizing the mass transfer are the mass transfer coefficient and interfacial area. Both of these parameters depend upon the flow conditions and nature and status of solid. Estimation of gas-liquid mass transfer rates also requires the knowledge of solubilities of absorbing and/or desorbing species and their variation with temperature.

In mass transfer studies; gas-liquid mass transfer is of most importance since in most of the reaction systems the gas-liquid is the rate-controlling step [1]. Indeed the gas-liquid mass transfer depends on two parameters, the mass transfer coefficient and interfacial area. Various researchers have contributed to enrich the studies on mass transfer coefficient and interfacial area in three phase systems. Jiasen Song, Caroline L. Hyndman, Rajesh K. Jakhe [2] studied the hydrodynamics and mass transfer in three phase fluidization. Weiguo Yang, Jinfu Wang, Tiefeng Wang studied the gas-liquid interfacial area and mass transfer in three phase circulating fluidized bed [3]. Dhanuka and Stepanek, 1980 [4], did experimental studies for volumetric mass transfer coefficient and interfacial area in three-phase fluidized bed.

For the determination of mass transfer coefficient and interfacial area various techniques like oxygen balance method, simultaneous absorption with chemical reaction of CO₂ and desorption of O₂, absorption with chemical reaction of CO₂, uses of various probes have been found in literature.

2. Determination of interfacial area and mass transfer coefficient

For the three-phase system, mass transfer is the main parameter for the design and operation of reactor. The gas-liquid mass transfer is characterized by two parameters, the gas-liquid mass transfer coefficient and gas-liquid interfacial area. It is found that in most of the reactions involving three phase the mass transfer is the rate controlling step so the determination of these parameters and influence operating parameters like, gas superficial

velocity, liquid superficial velocity, solid holdup, reactor size, bed expansion ratio on these parameters is of primary importance. Various researchers determined and studied these parameters using different methods. Some of these are discussed below.

2.1 Use of Optical Method for interfacial area determination:

Various methods have been adopted for determination of mass transfer coefficients and interfacial mass transfer area. For interfacial area determination, light scattering method, chemical method, and photographic method were adopted. It is found that light transmission technique gives better results followed by chemical method [4]. Weiguo Yang, Jinfu Wang, Tiefeng Wang, and Yong Jin [3] successfully studied mainly gas-liquid mass transfer in three phase circulating fluidized bed. They studied the gas-liquid mass transfer behavior in a three-phase circulating fluidized bed reactor of 140mm i.d. and 3.0m height. Using the oxygen dissolution method, the volumetric mass transfer coefficient kLa was obtained from the measured bulk concentration of the liquid phase by fitting to the axial dispersion model. The gas holdup and the distribution of bubble size in the bed are measured by a fiber optical probe system, then the gas-liquid interfacial area ' a ' and the mass transfer coefficient Kla are calculated. The influences of the main operating conditions, including superficial gas velocity, superficial liquid velocity and solid circulating rate, were studied systematically.

The experiments were carried out in a gas-liquid-solid three-phase fluidized bed shown in Fig. 1. The experimental apparatus consists of riser, liquid-solid separator, particle reservoir and liquid reservoir, etc. The riser is a vertical Plexiglas column of 140mm i.d. and 3.0m in height. Air, water and glass beads of 0.4mm are used as the gas, liquid and solid phases, respectively. The liquid pumped from the reservoir is divided into two streams and then fed into the bed, a primary stream fed into the bed bottom and a secondary stream below the exit of the circulating standpipe. Solid particles entrained from the top of the riser are separated from the liquid in a primary liquid-solid separator and returned to the reservoir. The particle-circulating rate is controlled by regulating the flow rate ratio between the two liquid streams.

The gas-liquid mass transfer indeed depends on gas-liquid interfacial area. First the bubble rise velocity is calculated by using the optical probe. Probe technique is an effective method to measure the bubble properties such as bubble size distribution and bubble rise velocity in three-dimensional three-phase fluidized beds. The fiber optic probe is applicable both to electric and non-electric system, and the compact structure reduces disturbance to the flow field giving more accurate result. These advantages make the fiber optic fiber preference in recent years. From the probe signal, we can only get the bubble rise velocity and bubble chord length distribution.

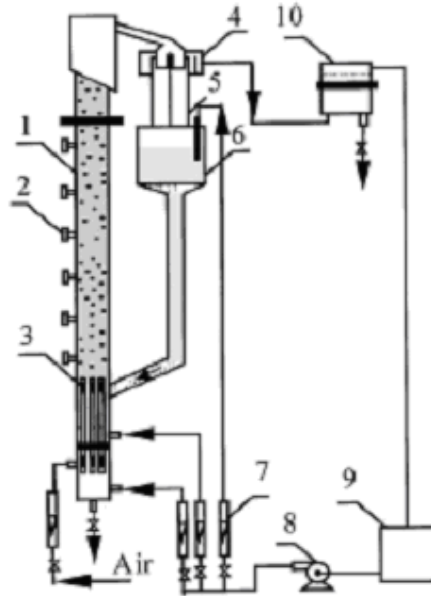


Fig. 1 Schematic diagram of experimental setup. 1- riser; 2- pressure tap; 3- gas-liquid distributor; 4- liquid solid separator; 5- particle metering tank; 6- particle reservoir; 7- flow meter; 8- liquid pump; 9- liquid reservoir; 10- secondary liquid solid separator. [3]

The algorithm inferring the bubble size distribution from the measured chord length distribution must be established. Some researchers proposed the algorithm for determining the size distribution of bubbles touching the probe, however, this bubble size distribution can not be directly used to determine the gas-liquid interfacial area with the given local gas holdup.

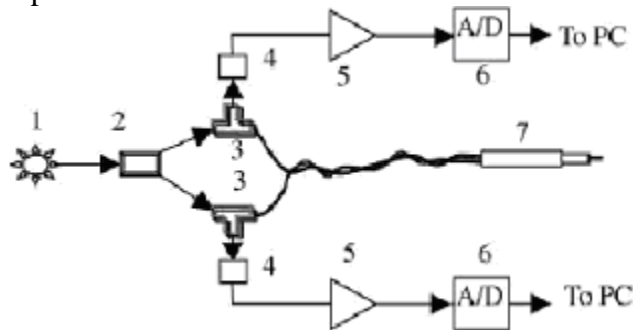


Fig. 2. Hardware structure of Fiber optic; 1- laser source; 2- Light splitters; 3- Fiber coupler; 4- Light detector; 5- Amplifier; 6- A/D Transducer; 7- Probe. [3]

The fiber optic probe connected to the bed-wall is movable in the radial direction so that the bubble behavior in different radial position can be measured. The hardware structure of probe is shown in Fig.2. By using the fiber optic probe the bubble rise velocity is determined. Bubble measurement using fiber optic probe is based on the refraction difference of the gas and liquid. The level of output signal is low when the probe fiber is in the liquid phase, and becomes high when the probe fiber pierces into a gas bubble. When the gas-liquid-solid mixture flows up concurrently, output signal containing bubble information is obtained, as shown in Fig.3. The downstream signal lags a little compared with the upstream signal due to the distance between the two fibers,

which is clearly in the locally enlarge signal Fig.3. The lag time can be determined by correlation method, and then, with the distance of the fibers, the bubble rise velocity can be calculated. They used the following equations for the determination of interfacial area.

$$a = \varepsilon_g \frac{6\alpha^2}{\pi} \left[\int_0^\infty P_s(d_b) d_b^3 dd_b \right]^{-1} \frac{\pi}{\alpha} \int_0^\infty P_s(d_b) d_b^2 dd_b$$

$$= \frac{6\alpha\varepsilon_g}{d_{va}}$$

Where, α is shape factor and ε_g is the gas holdup.

$$\alpha = \frac{1}{1 + 0.163 E_o^{0.757}} \quad Mo \leq 10^{-6}, E_o < 40$$

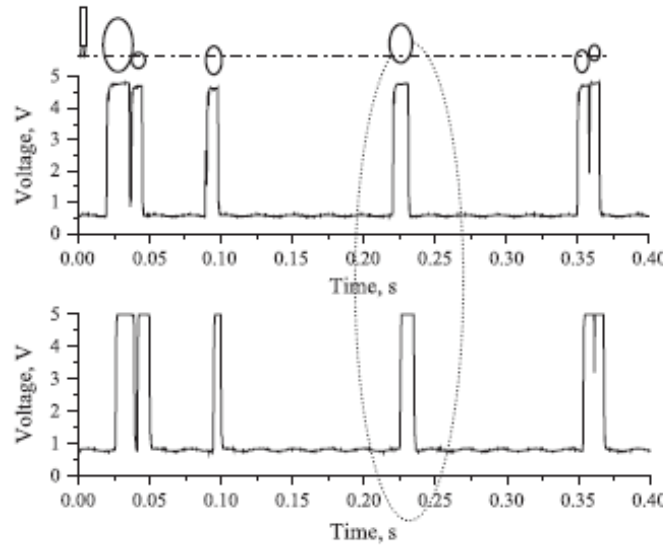


Fig. 3. Typical signal from optical probe [3]

The procedure can be summarized as, as shown in Fig. 4, the bubble peaks are first distinguished from the original data. Then the local gas holdup, the bubble rising velocity, the distribution of bubble chord length and the distribution of bubble size can be obtained after the arithmetic treatment of correlation, statistics and distributing transformation. The local gas holdup is determined by integrating the measured values over 0 to R . The distribution of bubble chord length is transformed to the distribution of bubble size by using the method of Liu et al. Based on the local gas holdup and the distribution of bubble size, the gas-liquid interfacial area can be calculated.

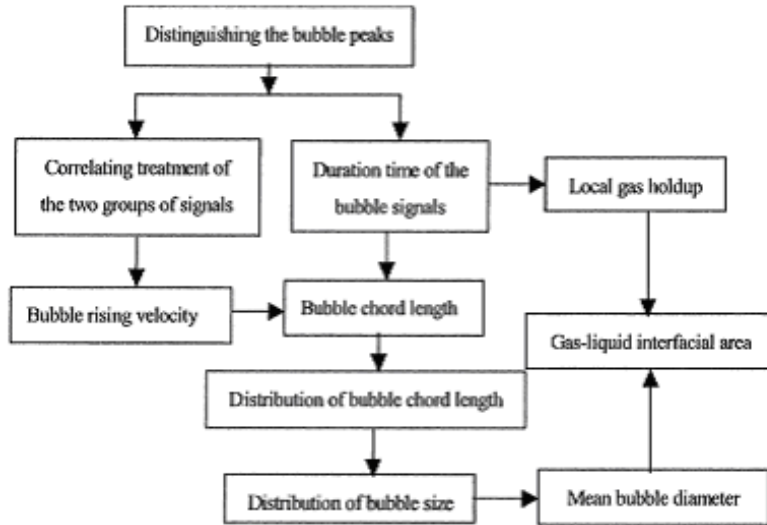


Fig.4.Program frame for data treatment process

2.2 Simultaneous measurement of interfacial area and mass transfer coefficient:

For determination of mass transfer coefficient various techniques were used like, Physical absorption/desorption, chemical method. Of these the chemical method is superior over the physical method as it dose not require knowledge of flow pattern and accurate analytical method. So chemical method is used widely over physical one. Robinson and Wilke (1974) [4] proposed a novel technique for the simultaneous determination of mass transfer coefficient and interfacial area. This technique involves simultaneous physical absorption of one gas from and absorption with chemical reaction of another solute gas into liquid phase. The rate of desorption of first species is used to evaluate the overall mass transfer coefficient and rate of chemical absorption with chemical reaction is then used to calculate interfacial area.

The original system proposed by Robinson and Wilke involves absorption of CO₂ from CO₂-N₂ mixture in to weak (< 0.1 M) KOH and desorbing O₂ from solution to CO₂-N₂ mixture. The change in O₂ concentration in KOH sol. is determined by dissolved oxygen probe and carbonate concentration is determined by potentiometer titration. For pseudo first order reaction the rate of absorption is given by

$$R_A \underline{a} = \underline{a} C_A^* (K_{LA}^2 + D_A K_2 C_o)^{0.5} \dots\dots\dots (1)$$

The rate of physical desorption is given by,

$$R_B \underline{a} = K_{LB} \underline{a} \Delta C_{B,m} \dots\dots\dots(2)$$

Where, $\Delta C_{B,m}$ is mean value of the difference in oxygen concentration between interfacial and bulk of liquid phase.

From penetration theory,

$$K_{LB} = K_{LA} (D_B/D_A)^{0.5} \dots\dots\dots (3)$$

So,

$$R_B \underline{a} = K_{LA} \underline{a} (D_B/D_A)^{0.5} \Delta C_{B,m} \quad \dots\dots(4)$$

To calculate interfacial area the Eq.1 can be rearranged as

$$\underline{a} = \{ [(R_A \underline{a} / C_A^*)^2 - (K_{LA} \underline{a})^2] / D_A K_2 C_o \}^{0.5} \quad \dots\dots\dots(5)$$

The calculation technique derived above involves

1. Experimental measurement of $R_A \underline{a}$ and $R_B \underline{a}$ with A referring to absorption of CO₂ and B referring to desorption of O₂.
2. Use of $R_B \underline{a}$ to calculate $K_{LB} \underline{a}$ by Eq.2 and $K_{LA} \underline{a}$ by Eq.4
3. The use of $R_A \underline{a}$ and $K_{LA} \underline{a}$ to calculate \underline{a} by Eq.5
4. The calculation of K_{LB} by dividing \underline{a} into $K_{LB} \underline{a}$

Dhanuka and Stepanek modify the original system due to low reaction rate and high ionic concentration change while absorption of CO₂. They used buffer solution of NaOH instead of KOH and used sodium hypo chloride to enhance the reaction rate and stabilize the ionic concentration. The series of experiments were carried out in perspex tube of 50 mm i.d. consisting two sections of 750 mm long each. Gas was introduced through the ring distributor placed at the bottom. The liquid is introduced through separate pipe so as to provide separate inlet for gas and liquid. Three sizes of glass ballotini were used of dia. 1.98 mm, 4.08 mm, and 5.86 mm. The superficial gas velocity was varied from 6.1 to 13.8 cm/s, while liquid superficial velocity was varied from 2-8 cm/s. The samples were taken at 620 mm from bottom. An arrangement was made so that no bubble is trapped in sample line.

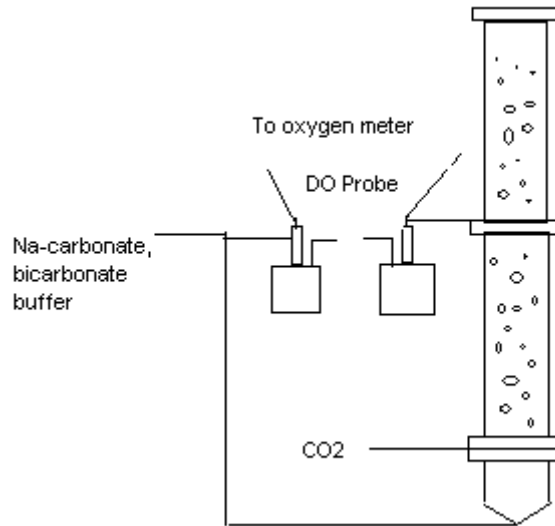


Fig. 5. Experimental Column [4]

The samples were pass through an airtight tube containing oxygen probe and then was collected for chemical analysis. The influence of various operating parameters on volumetric mass transfer coefficient and interfacial area was determined.

2.3 Oxygen Balance Method:

This technique depends on measurement of mass flow rates of aeration gas into and out of the oxygen-consuming reactor. The mass fraction of oxygen in the inlet and exhaust gas streams must also be determined (mass spectrometer, paramagnetic oxygen

analyzer) as well as the steady-state dissolved oxygen concentration in the fluid (dissolved oxygen electrode) [5].

The $K_L A_L$ is obtained from the oxygen balance:

$$F (X_i - X_o) = V_1 K_L A_L (C^* - C_l)$$

Where, F is the mass flow rate of gas, X_i and X_o are the mass fractions of oxygen in the gas (I-inlet, o- outlet), and V_1 is the volume of the fluid in the reactor. The above equation assumes no evaporation and it does not correct for possible evolution of carbon dioxide; however, the necessary corrections can be easily incorporated. For a constant volume continuous flow reactor, the above equation needs to be further modified to account for oxygen entering and leaving the reactor via the liquid streams. The oxygen balance method requires accurate measurements of gas flow rates and oxygen concentrations. The oxygen mass fraction in the inlet and outlet gas must differ measurably i.e., the oxygen consumption rate in the reactor should be relatively large for reliable $K_L A_L$ measurements. Under suitable conditions, the method is very reliable and it does not disturb the reactor by interrupting the air supply.

In the experimental technique, the gas of known oxygen concentration is bubbled through the reactor. The inlet as well as outlet concentration of oxygen in the gas is determined by any of the analyzer. The oxygen concentration at the inlet and outlet is determined using dissolved oxygen meter. Samples were taken at specified height for the analysis. Particles of different sizes were taken to study the influence of particle size on volumetric mass transfer coefficient. The gas and liquid superficial velocities were varied to mark their effect.

2.4 Mass transfer in biooxidation:

A.Venu Vinod, G. Venkat Reddy [6] studied the mass transfer in phenol biodegradation in fluidized bed bioreactor and developed correlations for mass transfer. In that he carried out series of experiments at different feed concentrations of phenol, airflow rates and feed flow rates. The mass transfer coefficient for phenol transfer from bulk phase to the surface of the biofilm on the solid particle was estimated from observed experimental data using the conservation equations. The mass transfer coefficient was found to be in the range of 0.0726×10^{-5} to $0.2012 \times 10^{-5} \text{ ms}^{-1}$. It was found to increase with increase in feed concentration, airflow rate and feed flow rate. A dimensionless correlation was also developed for the mass transfer coefficient in terms of Sherwood, Reynolds and Schmidt numbers. They used following equation for the determination of mass transfer coefficient based on the mass balance phenol from bulk phase to solid film.

$$N_p A_p K_s (S_b - S_i) = Q(S_f - S_b)$$

Where, N_p is number of bioparticles in the fluidized bed bioreactor, A_p is surface area of the bioparticle (m^2), K_s is mass transfer coefficient for the substrate (phenol) (m s^{-1}), S_b is steady state bulk phenol concentration in fluidized bed bioreactor (kg/m^3), S_i is phenol concentration at the biofilm surface (kg/m^3), Q is the feed flow rate to the fluidized bed bioreactor ($\text{m}^3 \text{ s}^{-1}$), S_f is phenol concentration in feed to fluidized bed bioreactor (kg/m^3)

Series of experiments were carried out to determine the rate of phenol biodegradation and mass transfer coefficient in a draft tube reactor of volume 2.67 liters. Air was introduced through an air sparger from the bottom of column. Plastic beads of average dia. 3.87 mm were used for immobilization of microorganisms. The operation is

carried out at constant PH. The oxygen concentration in the liquid phase is determined by DO meter. The airflow rate is varied from 1-10 lpm. A strain of microorganism *Pseudomonas putida* is used as a medium for phenol biodegradation. The culture is well prepared. The biofilm density was determined.

Four feed flow rates 396, 504,600 and 640 ml h⁻¹ were used. The effect of airflow rate has been examined at three airflow rates of 2, 3 and 4 lpm. The feed concentrations of phenol that have been used in the study were 50, 100, 150, 200 and 250 ppm.

5) Mass transfer in bubble column:

Bubble columns have been widely used in chemical process industries due to their simple construction, low cost and ease of operation. Meikap et.al. [7] studied the mass transfer in countercurrent multistage bubble column scrubber and predicted interfacial area in variable area multi-stage bubble column [8]. Chemical method was used for the analysis due to its advantages over the physical. The experimental bubble column consisted of vertical cylindrical Perspex column, 0.1905 m in dia. And 2.0 m long, fitted onto a fructo-conical bottom of mild steel. A sparger is fitted at the bottom so as to get uniform flow of gas. The column was divided into different stages by fitting different contraction and expansion discs. The column is made up of three sections by using these discs. The liquid is passed through inlet made at height of 1.8 m. The gas is passed through the sparger at bottom.

For the determination of mass transfer coefficient, the chemical rate of absorption of CO₂, diluted with air (6-10 mol % CO₂) in aqueous solution of sodium carbonate-bicarbonate buffer solution were used. The liquid is passed through the column and recycled back after proper adjustment of desired concentration. The liquid and gas samples were taken at the inlet and outlet after the steady state is achieved after 30 min. the Ph was maintained at 7.5-8.5. The gas samples were collected with the help of impingers containing known volume and concentration of BaCl₂ solution and aspirator bottles to find out inlet and outlet concentration of CO₂. Then the resulted masses from the impingers were analyzed by the volumetric method. The liquid samples were analyzed by standard methods of titration. The superficial liquid velocity and gas velocity were varied from 2.42×10^{-3} to 9.67×10^{-3} m/s and 0.106 to .19163 m/s.

3. Influence of operating parameters on mass transfer coefficient and interfacial area

3.1 Influence of superficial gas velocity:

Based on the measured gas holdup and bubble size distribution, the gas-liquid interfacial area is determined from the optical probe method, a shape factor of 0.8 is used. It can be seen in Figs. 6 and 7 that the superficial gas velocity has remarkable influence on gas-liquid mass transfer behavior in the three-phase circulating fluidized bed. Both the gas-liquid interfacial area and the gas-liquid mass transfer coefficient increase with increasing superficial gas velocity. The reason is that higher gas velocity increases the gas holdup and decreases the mean diameter of bubble, leading to the increase of gas-liquid interfacial area. In addition, the increase of gas velocity speeds up the rising

velocity of bubbles in the bed and enhances the turbulence of the liquid phase around the rising bubbles. The mass transfer resistance from the liquid film on the surface of bubbles to the liquid bulk decreases, then the gas-liquid mass transfer coefficient increases.

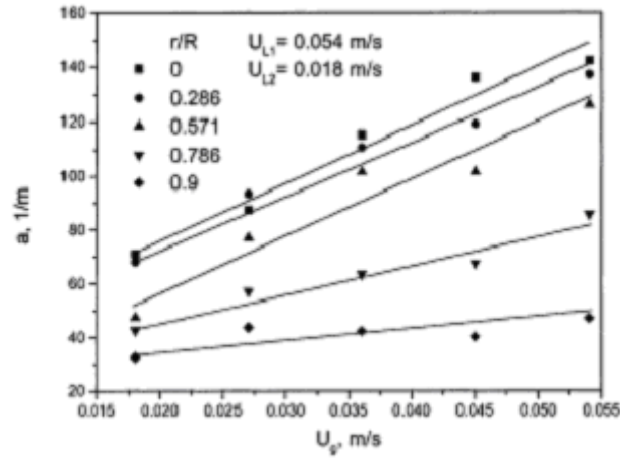


Fig.6. Influence of superficial liquid velocity on interfacial area

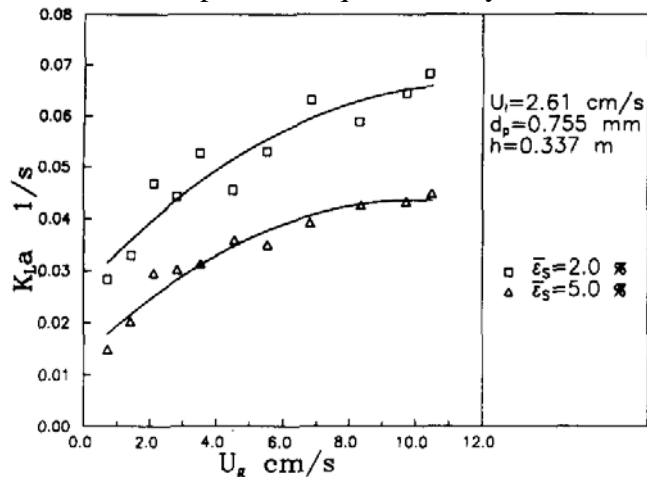


Fig. 7. Effect of superficial gas velocity on mass transfer coefficient for different solid loadings

3.2 Influence of liquid superficial velocity:

Figs.8. Illustrate the influence of superficial liquid velocity on the gas-liquid interfacial area. The superficial liquid velocity has a little influence on the gas-liquid interfacial area. The gas-liquid interfacial area of the wall region increases slightly with the increase of liquid velocity, but that of the center region changes little. As a result of small influence of liquid velocity on the mean bubble diameter, the variation of the gas-liquid interfacial area is determined by the influence of liquid velocity on the gas holdup. Increasing liquid velocity enhances the gas holdup of the wall region, so the gas-liquid interfacial area of the wall region increases. Fig.9. Shows, the mass transfer coefficient increases with superficial liquid velocity.

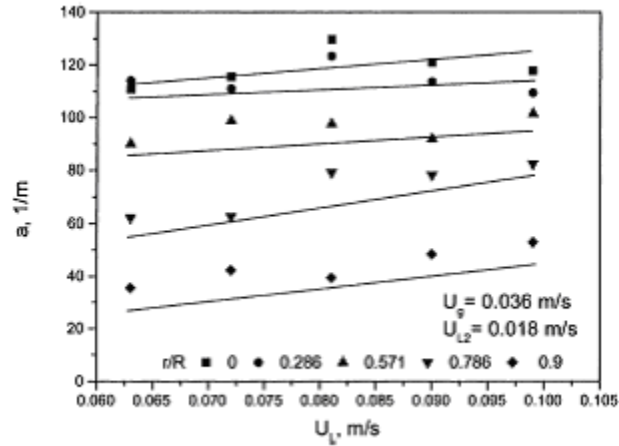


Fig.8.Effect of liquid superficial velocity on gas-liquid interfacial area at different radial position

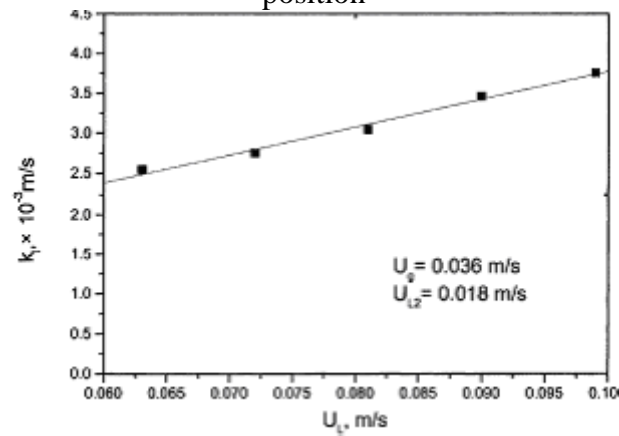


Fig.9. Effect of liquid superficial velocity on mass transfer coefficient.

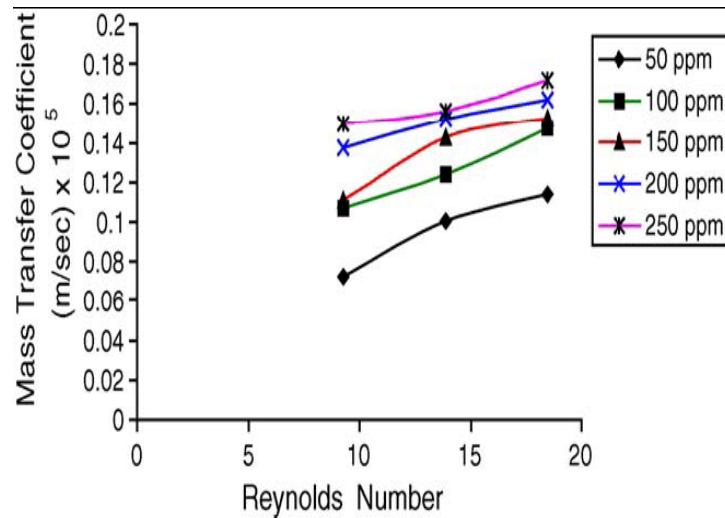


Fig. 10. Influence of Reynolds Number on mass transfer coefficient in phenol biodegradation.

3.3 Influence of solid holdup:

In the three-phase circulating fluidized bed, the solid holdup can be regulated through controlling the flow rate ratio of the main liquid flow and the secondary liquid flow to alter the particle-circulating rate. According to the work of Liang et al., the solid holdup is increased by the particle-circulating rate. It is seen that increasing particle circulating rate results in the increase of solid holdup and the decrease of gas–liquid interfacial area. The reason is that the increase of solid holdup leads to increasing the system apparent viscosity and the bubble coalescence will be increased consequently.

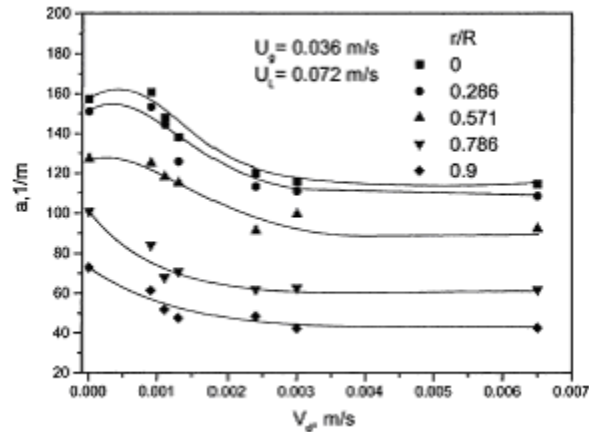


Fig. 11. The effect of particle circulating rate on the gas-liquid interfacial area at different radial position.

Conclusion:

Various measurement techniques have been adopted for the measurement of mass transfer coefficient and interfacial area in three-phase system. The compact structure of optical probe reduces disturbance to the flow field giving more accurate result for interfacial area determination and radial distribution of interfacial area can also be determined. The chemical method for mass transfer coefficient is more easy and accurate than physical. Simultaneous measurement gives better results as it determines both parameters under truly hydrodynamic and physico-chemical conditions. It is found that both interfacial area and mass transfer are strong functions of gas superficial velocity and increases with it but liquid superficial velocity has marginal influence on them. In case of bubble column, the mass transfer coefficient increases linearly with gas superficial velocity but remains almost constant thereafter. The mass transfer in bio-oxidation increases with Reynolds number and substrate concentration. The increased solid holdup increases the system apparent viscosity and the bubble coalescence reducing the interfacial area.

Nomenclature:

- a - gas-liquid interfacial area.
- ϵ_g - gas holdup.
- $P_s d_b$ - bubble size distribution
- d_b - bubble diameter
- α - Shape factor
- d_{va} - bubble Sauter diameter
- Eo - Evotvos number

M_o - the Morton number.
 R_A - rate of absorption of CO_2 .
 R_B - rate of absorption of O_2 .
 C_A^* - saturation concentration of CO_2
 K_{LA} – individual mass transfer coefficient
 D_A – diffusivity of CO_2 in liquid phase
 K_2 – reaction rate constant
 C_o – reactant concentration in liquid phase.

References:

1. Shah Y., (1979), Gas-liquid-solid Reactor Design, McGraw-Hill international Book Company
2. Jiasen S., Caroline L., Rajesh K., Kelly H., (1999), Fundamentals of hydrodynamics and mass transfer in a three-phase fluidized bed system, Chemical Engineering Science 54 (1999) 4967-4973
3. Yang W, Wang J, Wang T, Jin Y (Nov 1999), Experimental study on gas-liquid interfacial area and mass transfer coefficient in three-phase circulating fluidized beds, Chemical Engineering Journal 84 (2001), 485– 49
4. Dhanuka, Stepanek (1980), Simultaneous measurement of interfacial area and mass transfer coefficient in three phase fluidized bed, AIChE Journal, Vol: 26, Issue: 6, 1029-1038.
5. Kirk-Othmer Encyclopedia of Chemical Technology.
6. A.V. Vinod, G. V. Reddy (2006), Journal of Hazardous Materials B136 (2006) 727–734.
7. Meikap B.C., Kundu G. (2004), Mass transfer characteristics of a countercurrent multi-stage bubble column scrubber, Journal of chemical engineering Japan, Vol: 37, No: 10, 1185-1193.
8. Meikap B.C., Kundu G., Biswas M.N. (2001), Prediction of the interfacial area in variable area multistage bubble column, Ind. Eng. Chem. Res. 2001, 40, 6194-6200.
9. Chong Z., Hanns H (1995), Mass transfer in different flow regimes of three-phase fluidized beds, Chemical Engineering Science, Vol. 50, No. 10, pp. 1571-1578.
10. Yang W, Wang J, Wang T, Jin Y (1999), Gas-liquid mass transfer behavior in three-phase CFB reactors, Chemical Engineering Science 54 (1999) 5523- 5528.