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Gas–liquid mass transfer in slurry bubble systems
I. Mathematical modeling based on a single bubble mechanism

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Abstract

A gas–liquid mass transfer model for slurry bubble systems is established. It is based on the dynamic film mass transfer theory for a single bubble. The concentration in the liquid film is considered as a function of time t and radial position r. The analytical solution is obtained by Laplace transformation and the use of Danckwerts's age distribution function. The mass transfer coefficient k_L is deduced from the analytical solution. The influence of the model parameters: the surface renewal rate s and the thickness of the liquid film δ on the mass transfer coefficient k_L is simulated. The two parameters are correlated with the operating conditions such as temperature, pressure, superficial gas velocity and solid concentration to allow the model to be used to predict the interfacial mass transfer rate for slurry bubble systems.

Keywords: Slurry bubble system; Gas–liquid mass transfer; Mathematical model; Single bubble mechanism

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1. Introduction

Slurry bubble systems are widely used as three-phase reactors in chemical, petrochemical, biochemical and environmental processes [1]. The slurry reactor is the major reactor type for energy conversion processes such as Fischer–Tropsch synthesis, and liquid phase methanol (MeOH) and dimethylether (DME) synthesis. The liquid phase process makes possible the processing of large amounts of natural gas and coal into more suitable energy products. Due to limited world reserves in crude oil, the problem of a liquid fuel supply is becoming more serious and research on slurry bubble systems have received more attention in recent years.

The slurry bubble column is a commonly used reactor type for slurry bubble reaction systems. Generally, the presence of chemical reactions will enhance mass transfer across the liquid–solid interface and gas–liquid interfacial mass transfer becomes the determining step of the transfer process. Therefore, it is very important to describe quantitatively the gas–liquid mass transfer characteristics of slurry bubble columns for the optimum design and scale-up of slurry bubble column reactors.

In recent decades, many more attempts have been made by researchers in different fields for a better understanding of the mass transfer mechanism in slurry bubble systems. In a slurry system, the fine powder and the liquid phase can be treated as a pseudo-liquid phase because of the very low terminal velocity of the particles. Therefore, mass transfer models for gas–liquid systems such as the film theory (Whitman, 1923) [2] penetration theory [3] (Higbie, 1935) and surface renewal theory [4] are usually taken as a basis for modeling mass transfer in three-phase slurry bubble systems.

Nagy [5] used a one-dimensional heterogeneous model to predict mass transfer rates in three-phase systems. The model was based on a micro-scale mass balance and unsteady state film-penetration theory. A back flow model was established to describe mass transfer properties in multistage slurry bubble column by Tsuge et al. [6]. The model can be used to calculate concentration profiles, and to compare the gas–liquid mass transfer coefficients measured experimentally with those calculated by correlations used in the gas–liquid system, but it cannot determine the gas–liquid mass transfer coefficient k_L theoretically.

Tobajas [7] developed a mass transfer expression based on Higbie's penetration theory and Kolmogoroff's theory of isotropic turbulence to predict the volumetric mass transfer coefficient in an airlift marine sediment slurry reactor. Maretto [8] suggested a model for a slurry bubble column reactor for the Fischer–Tropsch process which can calculate the volumetric mass transfer coefficient k_La of large

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Nomenclature

a	specific gas–liquid interfacial area ($\mathrm{m^{-1}}$)
C_A	microscopic gas concentration in the liquid phase ($\mathrm{mol\,l^{-1}}$)
$\tilde{C}_\mathrm{A}$	Laplace-transformed gas concentration profile outside the bubble
C_i	gas concentration in the liquid phase at the gas–liquid interface ($\mathrm{mol\,l^{-1}}$)
C_L	macroscopic gas concentration in the slurry ($\mathrm{mol\,l^{-1}}$)
D_L	gas diffusion coefficient in the liquid ($\mathrm{m^2\,s^{-1}}$)
k_L	gas–liquid mass transfer coefficient ($\mathrm{m\,s^{-1}}$)
$k_\mathrm{L}a$	gas–liquid volumetric mass transfer coefficient ($\mathrm{s^{-1}}$)
$P(R)$	probability density function (1/mm)
r	radial position (m)
R	radius of bubble (m)
s	surface renewal constant ($\mathrm{s^{-1}}$)
t	time (s)

Greek symbols

δ	thickness of the mass transfer liquid film (m)
θ	microscopic time (s)
ψ	age distribution function ($\mathrm{s^{-1}}$)

and small bubbles, respectively. In the model they used two empirical formulas which correlated the ratio between $k_\mathrm{L}a$ and the gas hold-up with the diffusion coefficient. Shimizu et al. [9] proposed a mathematical model based on Higbie's penetration theory using bubble break-up and coalescence to calculate gas–liquid interfacial mass transfer coefficient $k_\mathrm{L}a$ in bubble columns. The application of this model is somewhat complicated for engineering practice because the volumetric mass transfer coefficient $k_\mathrm{L}a$ must be calculated by summing the $k_\mathrm{L}a$ of every bubble in the column.

Kittilsen et al. [10] developed a model of gas–liquid mass transfer for a laboratory slurry stirred reactor for olefin polymerization. They indicated that the renewal rate of the liquid surface controls the mass transfer rate, and is due to two different scales of eddies: the mean liquid flow at low stirring rates and the small-scale turbulence at high stirring rates. In the model the only parameter considered was the Reynolds number which only characterizes the influence of the flow state in the system.

Dudley [11] compared several models used in the calculation of the mass transfer coefficient k_L in bubble columns, including both empirical correlations and theoretical models, with his own experimental data, and indicated that Calderbank's correlation fitted his experimental data best. However, the Calderbank correlation does not include the influence of the superficial gas velocity on the mass transfer coefficient k_L. Cockx et al. [12] established a model to predict the mass transfer coefficient k_L in bubble columns based on a global correlation of the absorption coefficient. The mass transfer model was established by taking into account the interfacial momentum transfer velocity. The mass transfer coefficient k_L can be obtained if the interfacial velocity difference and the model parameters are known.

As mentioned above, a number of research works on gas–liquid mass transfer in gas–liquid and/or slurry bubble systems have been reported in the past. However, most of them are concerned with the measurements of the gas–liquid volumetric mass transfer coefficient and the interfacial area in the gas–liquid and slurry bubble systems. Some of them deal with mass transfer modeling but most mass transfer models are either confined to correlations within certain operating conditions of the studied systems, or take into account parameters with only limited influence. Up to now, there are no mathematical models that simulate the influence of the parameters of both the operating conditions and system characteristics on mass transfer in slurry bubble systems.

In this paper, a mathematical model for predicting the gas–liquid mass transfer rate is established for slurry bubble systems. It is based on the unsteady state film concept in the mass transfer with a single bubble. The model equation is solved by means of Laplace transformation and the solution to the partial differential equation is obtained analytically. The overall mass transfer coefficient across the gas and liquid phases in the slurry bubble systems can be calculated from the analytical solution and statistical averaging. The influence of the parameters of the model on the gas–liquid mass transfer coefficient k_L is simulated using the analytical solution. In the second part of this work, the validity of the model is verified and the model parameters are determined from measured mass transfer data from a slurry bubble column at high temperature and high pressures.

2. Mathematical modeling

The slurry phase in a slurry bubble column acts as a continuous phase and the gas phase in the system exists as a discrete phase in the form of individual bubbles of different sizes. The existence of particles directly affects the superficial viscosity of the slurry system which will influence the bubble size and the thickness and stability of the mass transfer film. Usually, the bubble size in the slurry system can be determined experimentally or from certain correlations with operating conditions. If we can set up relationships between mass transfer parameters and the characteristic parameters of the slurry, the mass transfer problem of a gas-slurry system can be treated as same as that of a gas–liquid system. Therefore, the mass transfer process between the gas and liquid phases can be determined from the mass transfer with individual bubbles in the system. In modeling the mass transfer process with a single bubble it is assumed that

- the shape of the bubble is a sphere of a given diameter,
- mass transfer resistance exists only in the liquid side of the liquid film,

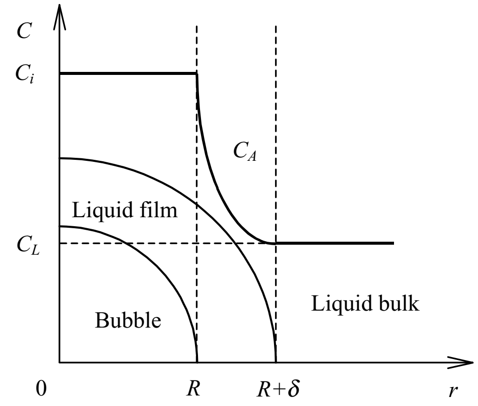

Fig. 1. The mass transfer mechanism in an unsteady state film of a single bubble.

- the liquid film or the interface between the bubble and the bulk phase has an age distribution due to bubble break up and coalescence and turbulence of the multiphase flow,
- mass transfer across the bubble interface is in unsteady state and
- the overall mass transfer rate can be obtained by calculating the bubble mass transfer rate with different bubble sizes and different age distributions at the interface and averaged statistically.

The mass transfer mechanism of a single bubble in a slurry bubble system is illustrated in Fig. 1. The bubble has a radius of R. Around the bubble surface is a liquid film of thickness δ. Mass transfer takes place in the liquid film and leads to a concentration profile in the liquid film. The mass transfer rate is enhanced if the liquid film is constantly renewed by liquid turbulence and bubble break up and coalescence. In order to estimate the mass transfer properly, different time scales are used, namely, a microscopic time coordinate θ for mass transfer in the liquid film and a macroscopic time coordinate t for mass transfer across the interface.

The mass transfer equation of a single bubble can be written in the microscopic spherical coordinate according to the unsteady state film concept as:

$$\frac{\partial C_\mathrm{A}}{\partial\theta} = D_\mathrm{L}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_\mathrm{A}}{\partial r}\right) \quad \text{in } R < r < R+\delta \tag{1}$$

with the following initial and boundary conditions:

$$\begin{cases} \theta = 0 & C_\mathrm{A} = C_\mathrm{L} \\ \theta > 0 & r = R \qquad C_\mathrm{A} = C_\mathrm{i} \\ & r = R+\delta \quad C_\mathrm{A} = C_\mathrm{L} \end{cases} \tag{2}$$

where D_L is the effective diffusion coefficient in the liquid phase, R the radius of the bubble, C_i the saturated concentration and C_L the concentration in the bulk phase.

The variation of concentration on the macroscopic time scale can be determined by the interfacial mass transfer rate and described by the following equation:

$$\frac{\mathrm{d}C_\mathrm{L}}{\mathrm{d}t} = k_\mathrm{L}a(C_\mathrm{L}^* - C_\mathrm{L}) \tag{3}$$

with the initial condition $t = 0$, $C_\mathrm{L} = 0$. Although both θ and t represent mass transfer times in the process, they are different time coordinates. θ is the mass transfer time from the beginning of contact of the single bubble with the liquid around it, whereas t is the contact time of the gas phase and the liquid time on a macroscopic time scale.

3. Solution of the mathematical model

Eq. (1) is a linear second-order partial differential equation which can be solved analytically by the appropriate treatment. First, Eq. (1) is rewritten as:

$$\frac{\partial C_\mathrm{A}}{\partial\theta} = D_\mathrm{L}\frac{2}{r}\frac{\partial C_\mathrm{A}}{\partial r} + D_\mathrm{L}\frac{\partial^2 C_\mathrm{A}}{\partial r^2} \quad \text{in } R < r < R+\delta \tag{4}$$

This partial differential equation can be solved more easily by Laplace transformation [13,14]. Using the Laplace transform, $\tilde{C}_\mathrm{A}(r,s) = \int_0^{+\infty} C_\mathrm{A}(r,\theta)\,\mathrm{e}^{-s\theta}\,\mathrm{d}\theta$, Eq. (5) is transformed into an ordinary differential equation. The transformed equation is

$$\frac{\partial^2\tilde{C}_\mathrm{A}(r,s)}{\partial r^2} + \frac{2}{r}\frac{\partial\tilde{C}_\mathrm{A}(r,s)}{\partial r} - \frac{s}{D_\mathrm{L}}\tilde{C}_\mathrm{A}(r,s) = -\frac{C_\mathrm{L}}{D_\mathrm{L}} \tag{5}$$

where s is the transformation variable. It should be noted that the initial condition of Eq. (1), $C_\mathrm{A}(r,0) = C_\mathrm{L}$, has been used in the transformation of the accumulation term of Eq. (1). The boundary conditions are transformed into the following form:

$$\begin{cases} r = R & \tilde{C}_\mathrm{A} = \dfrac{C_\mathrm{i}}{s} \\ r = R+\delta & \tilde{C}_\mathrm{A} = \dfrac{C_\mathrm{L}}{s} \end{cases} \tag{6}$$

Eq. (5) is a second-order nonhomogeneous ordinary differential equation. Its general solution is the sum of the general solution of its corresponding homogeneous differential equation and a particular solution, that is

$$\tilde{C}_\mathrm{A}(r,s) = \tilde{C}_{\mathrm{A},1}(r,s) + \tilde{C}_{\mathrm{A},2}(r,s) \tag{7}$$

The general solution of the corresponding homogeneous differential equation of Eq. (5) is obtained by solving Eq. (5) with the right side set to zero. The solution is

$$\tilde{C}_{\mathrm{A},1}(r,s) = \frac{C_1}{r}\cos\left(\frac{r}{D_\mathrm{L}}\sqrt{-sD_\mathrm{L}}\right) + \frac{C_2}{r}\sin\left(\frac{r}{D_\mathrm{L}}\sqrt{-sD_\mathrm{L}}\right) \tag{8}$$

where C_1 and C_2 are two arbitrary integration constants.

It can also be proved that C_L/s is a particular solution of Eq. (5), that is, $\tilde{C}_{\mathrm{A},2}(r,s) = C_\mathrm{L}/s$. According to Eq. (7) the general solution of Eq. (8) can be written as:

$$\tilde{C}_A(r,s) = \frac{1}{s}C_L + \frac{C_1}{r}\cos\left(\frac{r}{D_L}\sqrt{-sD_L}\right) + \frac{C_2}{r}\sin\left(\frac{r}{D_L}\sqrt{-sD_L}\right) \tag{9}$$

The integration constants C_1 and C_2 are found by solving the algebraic equation obtained using Eq. (9) and the boundary conditions of Eq. (6). These two constants are:

$$C_1 = R\frac{(C_i - C_L)\{\sin[(R/D_L)\sqrt{-sD_L}] + \tan[(\delta/D_L)\sqrt{-sD_L}]\cos[(R/D_L)\sqrt{-sD_L}]\}}{s\tan[(\delta/D_L)\sqrt{-sD_L}]} \tag{10}$$

$$C_2 = R\frac{(C_L - C_i)\{\cos[(R/D_L)\sqrt{-sD_L}] - \tan[(\delta/D_L)\sqrt{-sD_L}]\sin[(R/D_L)\sqrt{-sD_L}]\}}{s\tan[(\delta/D_L)\sqrt{-sD_L}]} \tag{11}$$

Eq. (9) is the profile of the Laplace transformed concentration. The spatial concentration profile in the liquid film around the bubble surface at different times θ can obtained if the inverse Laplace transformation of Eq. (9) is possible. Here, we are interested in the mass transfer coefficient in order to characterize the properties of the interfacial mass transfer and not on the concentration profile itself. It is shown below that when the age distribution function for the liquid film is properly chosen, there is no need to perform the inverse Laplace transformation of Eq. (9), which is a very complicated mathematical problem, to deduce the mass transfer coefficient k_L across the interface.

4. Mass transfer coefficient k_L of the liquid film

The instantaneous point mass transfer rate across the interface between the liquid bulk and the bubble is given by:

$$N_A(\theta)|_{r=R} = -D_L\left.\frac{\partial C_A}{\partial r}\right|_{r=R} \tag{12}$$

The average mass transfer rate across the interface between the gas and liquid phase $\bar{N}_A|_{r=R}$ is an integral of the instantaneous point mass transfer rates at various film locations with different film age. It can be calculated using the surface age distribution function proposed by Danckwerts [4], $\psi(\theta) = s\,e^{-s\theta}$, as follows:

$$\bar{N}_A|_{r=R} = \int_0^\infty N_A(\theta)|_{r=R}\,\psi(\theta)\,d\theta = k_L(R)(C_i - C_L) \tag{13}$$

If we identify the Laplace transformation variable s with the parameter of the Danckwerts age distribution function s, the average mass transfer rate can be deduced using the definition of the Laplace transform:

$$\begin{aligned}\bar{N}_A|_{r=R} &= \int_0^\infty N_A(\theta)|_{r=R}\,\psi(\theta)\,d\theta \\ &= \int_0^\infty -D_L\left.\frac{\partial C_A}{\partial r}\right|_{r=R} s\,e^{-s\theta}\,d\theta \\ &= -D_L\left.\frac{\partial\int_0^\infty C_A(r,\theta)s\,e^{-s\theta}\,d\theta}{\partial r}\right|_{r=R} \\ &= -sD_L\left.\frac{\partial\tilde{C}_A(r,s)}{\partial r}\right|_{r=R}\end{aligned} \tag{14}$$

By comparing Eqs. (13) and (14) we can write the mass transfer coefficient in the liquid film in the form:

$$k_L(R) = -sD_L\frac{\partial\tilde{C}_A(r,s)/\partial r|_{r=R}}{C_i - C_L} \tag{15}$$

The final expression of the mass transfer coefficient k_L is obtained by substituting Eq. (9) into Eq. (15) and simplification using the mathematical relationship:

$$\mathrm{sh}(x) = -i\sin(ix), \qquad \mathrm{ch}(x) = \cos(ix) \tag{16}$$

Thus, the gas–liquid mass transfer coefficient k_L of a single bubble is expressed as:

$$k_L(R) = \frac{R\sqrt{sD_L}\,\mathrm{ch}((\delta/D_L)\sqrt{sD_L}) + D_L\,\mathrm{sh}((\delta/D_L)\sqrt{sD_L})}{R\,\mathrm{sh}((\delta/D_L)\sqrt{sD_L})} \tag{17}$$

Eq. (17) indicates that the gas–liquid mass transfer coefficient in a slurry bubble system is independent of concentration and time. The main factors influencing the gas–liquid mass transfer coefficient are the bubble radius R, film thickness δ and surface renewal rate s. It can be seen clearly from Eq. (17) that the gas–liquid mass transfer coefficient is enhanced with a decrease of the bubble size. Small bubble means a large curvature of the bubble surface which results in a large gradient of concentration in the liquid film. As a result, the mass transfer coefficient increases with a decrease in bubble size. In addition, decreasing the bubble size increases the mass transfer interface between the gas and slurry phase, which will also enhance the mass transfer process.

5. Overall mass transfer coefficient

Based on the analytical solution of the mass transfer coefficient of a single bubble, the overall average mass transfer coefficient k_L of the whole slurry bubble system can be calculated by statistical integration using the distribution of bubble sizes $P(R)$ measured experimentally

$$k_L = \int_0^{R_{\max}} k_L(R)P(R)\,dR \tag{18}$$

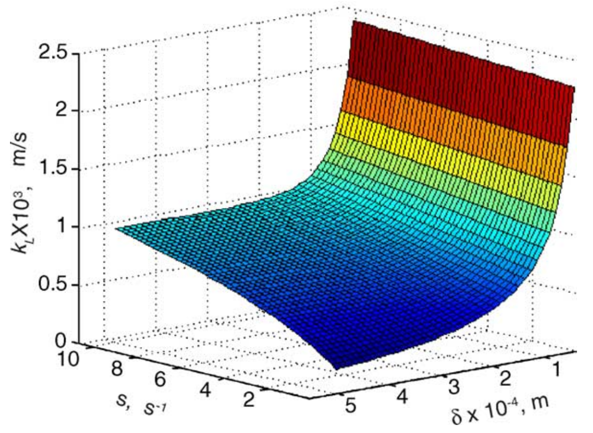

Fig. 2. Relationship between the mass transfer coefficient and the model parameters s and δ.

Fig. 2 shows the relationships between the mass transfer coefficient k_L and the model parameters s and δ under the condition of $R = 3\,\mathrm{mm}$ graphically. It can be seen that the thickness of the mass transfer liquid film δ has a large influence on the mass transfer coefficient and the surface renewal rate s has less influence with certain values of δ. With an increase in δ, calculated k_L values tend to decrease and this trend is quite distinct when δ is small. It is obvious from the mass transfer mechanism that increasing δ will increase the mass transfer resistance and lead to a decrease in k_L. Smaller δ is conducive to mass transfer.

In the surface renewal theory of Danckwerts [4], the model parameter s is defined in the age distribution function, $\psi(\theta) = s\,\mathrm{e}^{-s\theta}$, where $\psi(\theta)$ is the age of the liquid film on the bubble surface. Then the average age of the film on the bubble surface is $\int_0^\infty \theta\psi(\theta) = 1/s$. Therefore, s is the renewal rate of the liquid film on the bubble surface as it is replaced by fresh liquid and it characterizes the extent of surface renewing. It can be concluded that the mass transfer coefficient k_L will increase with an increase in s and a larger surface renewal extent, as illustrated in Fig. 2. However, it can be seen from the calculated results that the calculated k_L is almost insensitive to s when δ is less than a certain value. The influence on k_L becomes distinct when δ is larger. This indicates that the mass transfer resistance is mainly determined by δ and s influences the mass transfer coefficient k_L only when d is larger than a certain value.

6. Conclusions

A gas–liquid mass transfer model is established for slurry bubble systems that is based on the concept of the unsteady state film of a single bubble. An analytical solution for the mathematical model is obtained by Laplace transform. An expression for the mass transfer coefficient k_L is derived using the Danckwerts' surface age distribution function. The influences of the model parameters on the gas–liquid mass transfer coefficient are illustrated. The mass transfer model developed in this paper can be used to predict the gas–liquid mass transfer coefficient k_L for slurry bubble systems when the two model parameters are correlated with the operating conditions in the reactor. These correlations are determined by experiments.

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