Gas-Liquid Mass Transfer in a Slurry Bubble Column at High Slurry Concentrations and High Gas Velocities

By *Chippla O. Vandu, Ben van den Berg,* and *Rajamani Krishna**

The volumetric mass transfer coefficient k_La in a 0.1 m-diameter bubble column was studied for an air-slurry system. A C_9-C_{11} *n*-paraffin oil was employed as the liquid phase with fine alumina catalyst carrier particles used as the solid phase. The *n*-paraffin oil had properties similar to those of the liquid phase in a commercial Fischer-Tropsch reactor under reaction conditions. The superficial gas velocity U_G was varied in the range of 0.01 to 0.8 m/s, spanning both the homogeneous and heterogeneous flow regimes. The slurry concentration ε_S ranged from 0 to 0.5. The experimental results obtained show that the gas hold-up ε_G decreases with an increase in slurry concentration, with this decrease being most significant when $\varepsilon_S < 0.2$. k_La/ε_G was found to be practically independent of the superficial gas velocity when $U_G > 0.1$ m/s is taking on values predominantly between 0.4 and 0.6 s^{-1} when $\varepsilon_S = 0.1$ to 0.4, and 0.29 s^{-1}, when $\varepsilon_S = 0.5$. This study provides a practical means for estimating the volumetric mass transfer coefficient k_La in an industrial-size bubble column slurry reactor, with a particular focus on the Fischer-Tropsch process as well as high gas velocities and high slurry concentrations.

1 Introduction

The use of bubble columns for carrying out a wide range of industrial reactions is well documented in the literature [1]. Of particular interest, however, is the utilization of these reactors for gas-to-liquids applications such as the Fischer-Tropsch (FT) synthesis, by which natural gas is converted into liquid fuels. Given the depletion of global crude oil reserves and the abundance of remote gas fields, gas-to-liquids processes could eventually become very significant in the supply of transportation fuels. It is widely accepted that the bubble column slurry reactor is the best choice of reactor type for large-scale plants with capacities of the order of 40,000 bbl/day of liquid hydrocarbon product [2–6]. Though the superficial gas velocity U_G in the FT bubble column slurry reactor is in the range of 0.1 to 0.3 m/s, depending on the catalyst activity and catalyst concentration in the slurry phase [7], advances in reactor design and catalyst technology could see the use of much higher gas throughputs in the near future. For high reactor productivities, the highest slurry concentrations consistent with catalyst handling should be used. In practice, the volume fraction of the slurry phase ε_S has been reported as being of the order of 0.15 to 0.3 [7,8]. For the FT process to be economically viable, high syngas conversions are required, say exceeding 95 %. Achieving such high conversions could require operating with as high a slurry phase concentration as possible. Reliable design of the reactor to achieve such high conversion levels requires reasonably accurate information on key design parameters such as the gas hold-up ε_G and the volumetric mass transfer coefficient k_La. While there have been several experimental studies in slurry bubble columns (for literature surveys, see [9,10]), most of the published work is restricted to values of U_G less than 0.2 m/s with low slurry concentrations.

The main objective of this paper is the generation of data on the gas-liquid volumetric mass transfer coefficient relevant to the FT process. To do this, a predominantly C_9-C_{11} *n*-paraffin oil fraction with properties (density, viscosity, surface tension) similar to those of the liquid phase in the commercial FT reactor under reaction conditions was used. Fine alumina catalyst carrier particles were utilized as the solid phase. The slurry concentration was incremented in the range of $\varepsilon_S = 0$ to 0.5, with the superficial gas velocity spanning the range of $U_G = 0.01$ to 0.8 m/s. The data generated from this study will be useful in scaling up a slurry bubble column for the FT process.

2 Experimental

Experiments were conducted in a 0.1 m-diameter polyacrylate bubble column. The set-up is shown in Fig. 1. The column had a 1 mm-thick brass plate gas distributor with perforated holes of 0.5 mm diameter arranged on a triangular pitch of 7 mm. This gave rise to a total of 199 holes on the distributor plate. The air flow rate into the column was regulated by the use of one of four precalibrated Sho-Rate Brooks rotameters aligned in parallel. The flow of nitrogen (nitrogen was employed for stripping out dissolved oxygen from the liquid phase in the column) was controlled by the use of a manually operated control valve connected to the bottom of the column. A venting system attached to the top of the column safely led and disposed of evaporating liquid.

In all experiments carried out, air was used as the gas phase with a predominantly C_9-C_{11} *n*-paraffin mixture cut used as the liquid phase. Sasol PURALOX ScCa 5/170, an alumina-based catalyst particle carrier, was employed as the solid phase. Properties of the paraffin mixture and alumina particles utilized are given in Tabs. 1 and 2. The properties

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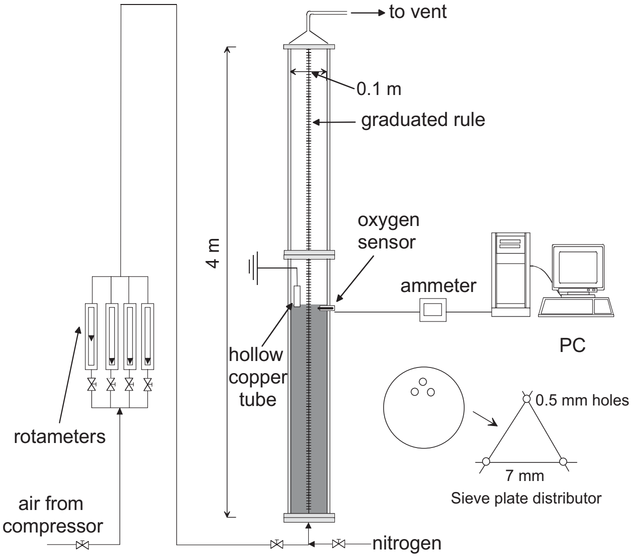

Figure 1. Experimental set-up of the 0.1 m-diameter slurry bubble column.

Table 1. Properties of paraffin oil at 298 K.

Density	726 kg/m^3
Viscosity	0.85 mPa s
Surface tension	23.2 mN/m
Diffusivity of oxygen	$3.69 \cdot 10^{-9}$ m^2/s
Composition	$\geq C_8$: 3.3 %; C_9: 36.3 %; C_{10}: 34.5 %; C_{11}: 23.8 %; $> C_{12}$: 1.9 %

Table 2. Properties of alumina catalyst carrier.

Al_2O_3 content	98 %
Skeletal density	3900 kg/m^3
Specific surface area	192 m^2/g
Particle porosity	70 %
Particle size distribution	10 % < 10 µm; 50 % < 16 µm; 90 % < 39 µm

of the catalyst carrier are similar to those envisaged for use in a commercial FT reactor. The slurry concentration ε_S was varied in the range 0, 0.1, 0.2, 0.3, 0.4, and 0.5. Slurry concentration is defined throughout this paper as the volume fraction of solids in gas-free slurry. The pore volume of the catalyst particles, which is liquid-filled during experiments, was counted as being part of the solid phase. At the start of each experimental investigation, the clear liquid (or slurry) height H_0 was set at 1.45 m. The liquid phase was regularly replenished during experiments to make up for the amount lost as a result of evaporation.

The gas hold-up was determined by visual measurements. In order to do this, the gas flow rate for a given experimental run was adjusted using one flowmeter at a time. Sufficient time was given for steady state to be reached in the column after which the dispersion height was recorded. The gas hold-up is defined as[1]:

$$\varepsilon_G = \frac{H - H_0}{H} \tag{1}$$

where H_0 is the ungassed column height and H is the column dispersion height resulting from the presence of gas bubbles.

The gas-liquid volumetric mass transfer coefficient $k_L a$ was determined by means of a dynamic oxygen absorption technique. A YSI Model 5331 oxygen sensor, inserted at a point just beneath the ungassed bed height (see Fig. 1) was used to measure the change in dissolved oxygen concentration. Readings from the sensor were fed to a personal computer (PC) that had an analogue-to-digital converter card, through an ammeter (see Fig. 1). The change in dissolved oxygen concentration was reflected as a change in electrical current displayed on the ammeter. The oxygen sensor was made sensitive to the presence of dissolved oxygen by applying a 0.13 g/mL KCl solution between its tip and an outer membrane made of Teflon. Before the start of each experimental run, the membrane surrounding the tip of the sensor was changed and the sensor time constant determined. This constant corresponds to an inherent delay in readings obtained due to the fact that the oxygen sensor has a finite response time. In determining the sensor constant, two continuously stirred glass beakers filled with the *n*-paraffin oil cut were used. Nitrogen was continuously bubbled into the first beaker and air into the other such that the liquid phases in both beakers became completely saturated with dissolved gases over time. The sensor was placed in the nitrogen-saturated liquid and after registering a negligible oxygen concentration, was instantaneously transferred to the oxygen-saturated liquid.

Based on the assumption of a perfectly mixed liquid phase, the oxygen concentration value indicated by the sensor once transferred to the oxygen-saturated liquid is given by:

$$\frac{dC_{sensor}}{dt} = k_{sensor}\left(C_L^* - Csensor\right) \tag{2}$$

where k_{sensor} is the sensor time constant. Integrating Eq. (2) gives:

$$\frac{C_{sensor}}{C_L^*} = 1 - e^{-k_{sensor}t} \tag{3}$$

A typical sensor response with the fit obtained is shown in Fig. 2a). The sensor constant values obtained based on all experiments carried out ranged from 0.76 to 1.3 s^{-1}, with the average value being 1 s^{-1}. In a previous paper [11], it was demonstrated that the presence of alumina catalyst carrier particles in the *n*-paraffin mixture used has no noticeable effect on the value of k_{sensor}.

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[1] List of symbols at the end of the paper.

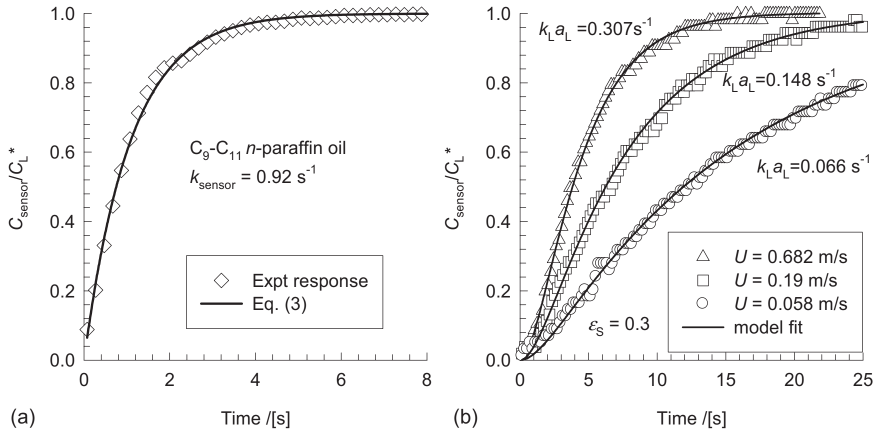

Figure 2. (a) Typical sensor response obtained in the C_9-C_{11} *n*-paraffin oil system, with a resulting k_{sensor} value of 0.92 s^{-1}, (b) oxygen absorption dynamics for C_9-C_{11} *n*-paraffin slurry with $\varepsilon_S = 0.3$ at different gas velocities.

For the determination of k_La in the slurry bubble column, dissolved oxygen was stripped from the liquid phase to a negligible concentration by the use of nitrogen sparged through the gas distributor. After the stripping operation, a step input of air was introduced into the column, with the uptake of oxygen into the liquid phase continuously monitored by the oxygen sensor. Sufficient time was given in each experimental run for the oxygen saturation concentration in the liquid C_L^* to be reached. With the assumptions of a perfectly mixed liquid and negligible oxygen depletion from the gas bubbles, the rate of oxygen uptake is described by:

$$\frac{dC_L}{dt} = k_L a_L \left(C_L^* - C_L\right) \quad (4)$$

where k_La_L is the volumetric mass transfer coefficient per unit volume of *liquid* in the bubble column. The assumption of a well-mixed liquid phase was verified to be a good one for the experimental conditions reported in this paper due to the high degree of liquid circulations in the churn-turbulent regime. The sensor delay equation, resulting from the finite response time of the oxygen sensor, is given by:

$$\frac{dC_{sensor}}{dt} = k_{sensor}\left(C_L - C_{sensor}\right) \quad (5)$$

Analytical solution of Eqs. (4) and (5) yields:

$$\frac{C_{sensor}}{C_L^*} = 1 - \frac{1}{k_{sensor} - k_L a_L}\left[k_{sensor} e^{-k_L a_L t} - k_L a_L e^{-k_{sensor} t}\right] \quad (6)$$

The volumetric mass transfer coefficient per unit volume of *dispersion* (gas + liquid + solid) k_La is obtained from:

$$k_L a = k_L a_L \left(1 - \varepsilon_G\right)\left(1 - f_S \varepsilon_S\right) \quad (7)$$

where f_S is the volume fraction of the solid particles due to the solid skeleton structure (i.e., not taking into account the solid pore volume contribution). Gas-liquid mass transfer can occur in the pores of the solid particles, which become filled with liquid during experiments. Typical oxygen absorption curves are shown in Fig. 2b) for $\varepsilon_S = 0.3$ at different gas velocities. Even at the highest gas velocities used in this study, the oxygen absorption dynamics were much slower than the sensor dynamics, meaning that suitably accurate volumetric mass transfer coefficient values could be obtained. Nonetheless, the sensor dynamics was routinely accounted for by the use of Eq. (6).

The use of alumina-based particles as the solid phase posed a challenge in the operation of the slurry bubble column described in this paper. Alumina particles are poor conductors of electricity but excellent dielectric materials, i.e., they support the creation of electrostatic fields. One consequence of this property is that alumina particles can become fairly good conductors of electricity in the presence of large electrostatic fields. As a result of this, alumina particles become deposited on the tip of the oxygen sensor, severely affecting its ability to detect the presence of dissolved oxygen. This problem was fully overcome by inserting a 50 mL hollow copper tube into the bubble column (see Fig. 1). This tube, which was properly earthed using a thin copper wire, provided a large conducting surface compared to the tip of the oxygen sensor. In this way, during experiments, the alumina catalyst carrier particles were deposited on the surface of the copper tube but not at all on the oxygen sensor. The additional increase in dispersion volume resulting from the presence of the hollow copper tube was corrected during gas hold-up experiments.

3 Results and Discussion

In Fig. 3a), the gas hold-up is shown as a function of superficial gas velocity. As the volume fraction of solid particles in the column is increased, the gas hold-up decreases for a given U_G. This is consistent with earlier findings on gas hold-up in paraffin oil slurries [12, 13] and can be attributed to the fact that as the slurry concentration increases, the tendency of small bubbles to coalesce and form large bubbles is enhanced. Large bubbles rise through the column with higher velocities than small bubbles, resulting in a decrease in the gas hold-up for a given U_G. It is also observed that for ε_S

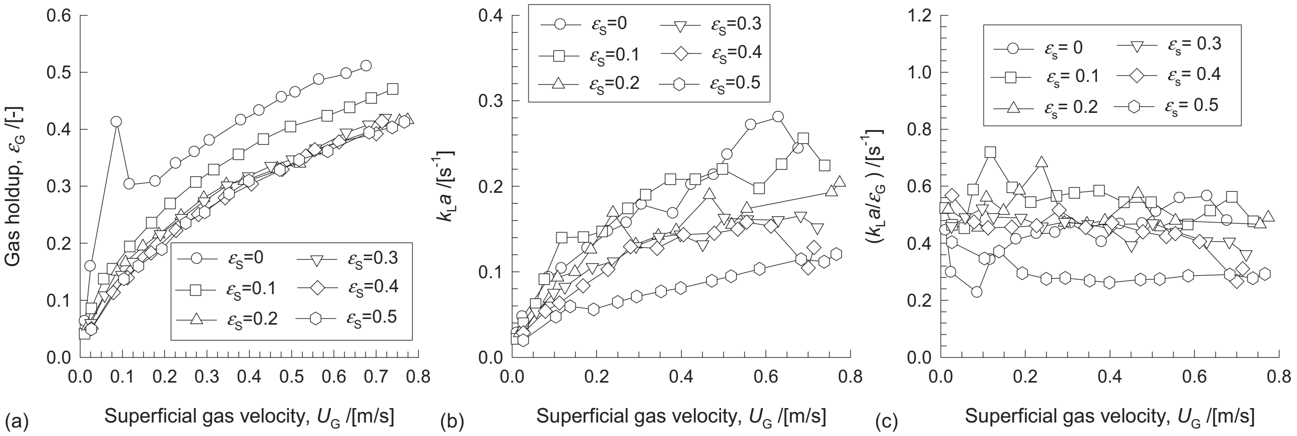

Figure 3. (a) Influence of superficial gas velocity U_G on (a) gas hold-up ε_G, (b) volumetric mass transfer coefficient k_La, and (c) k_La/ε_G for slurry concentrations ε_S = 0, 0.1, 0.2, 0.3, 0.4, and 0.5.

≥ 0.2, gas hold-up values tend to be practically indistinguishable at a given superficial gas velocity when U_G is in excess of 0.4 m/s.

The influence of slurry concentration on k_La is shown in Fig. 3b). While the discernable trend indicates that k_La decreases with an increase in ε_S over the entire data range, data for $\varepsilon_S = 0$, 0.1 and 0.2 when $U_G < 0.3$ m/s overlap, indicating virtually no slurry concentration dependence in this region. For $\varepsilon_S = 0.5$, however, k_La is consistently lower than for all other slurry concentrations employed. In published literature studies on the influence of slurry concentration on k_La [10, 11, 14], a variety of trends have been observed, depending on the slurry concentration range and the nature of the particles employed. None of these studies, however, attempted to cover both the wide range of superficial gas velocities and high slurry concentration values presented in this paper. Fig. 3c) shows a plot of k_La/ε_G versus U_G for the various slurry concentrations employed in this study. This plot is interesting because it shows that for superficial gas velocities $U_G > 0.1$ m/s, the value of k_La/ε_G is practically independent of U_G and has values in the range of 0.4 to 0.6 s^{-1} when ε_S = 0.1 to 0.4. The value of k_La/ε_G, when $\varepsilon_S = 0.5$, is significantly lower, with a mean value of 0.29 s^{-1} when $U_G > 0.1$ m/s.

The constancy of k_La/ε_G in the heterogeneous flow regime, i.e., when $U_G > 0.1$ m/s, can be attributed to the fact that the effective bubble diameter in this regime is independent of the gas velocity, as demonstrated by [15] using high-speed video imaging experiments in a rectangular slurry bubble column. This can further be rationalized if one takes into account the fact that the frequent coalescence and break-up of large bubbles causes the effective bubble diameter to be maintained at a constant value, as demonstrated by [16] on the basis of video imaging experiments in a 2D slurry bubble column.

4 Conclusions

The gas hold-up and volumetric mass transfer coefficient in a slurry bubble column have been studied with a predominantly C_9-C_{11} *n*-paraffin oil as the liquid phase and alumina catalyst carrier particles as the solid phase. The superficial gas velocity U_G covered a span of 0.01 to 0.8 m/s, with the slurry concentration ε_S ranging from 0.1 to 0.5 in increments of 0.1. Increasing the slurry concentration tends to decrease the gas hold-up, with this effect being less pronounced when $\varepsilon_S \geq 0.2$ and $U_G > 0.4$ m/s. A very interesting discovery is that k_La/ε_G is independent of the superficial gas velocity for U_G > 0.1 m/s, varying in the range of 0.4 to 0.6 s^{-1} when ε_S = 0.1 to 0.4 and taking on a mean value of 0.29 s^{-1} when $\varepsilon_S = 0.5$. Though the constancy of k_La/ε_G in the heterogeneous regime has previously been reported for slurry systems, previous studies were restricted to lower slurry concentrations and gas velocities. The findings presented in this paper will thus be very useful for slurry bubble column reactor scale-up by providing a useful guide for estimating the volumetric mass transfer coefficient at high gas velocities and high slurry concentrations, with a particular focus on the FT process.

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Symbols used

a	[m^{-1}]	gas-liquid interfacial area per unit dispersion (gas + liquid + solid) volume
a_L	[m^{-1}]	gas-liquid interfacial area per unit liquid volume
C_L	[arbitrary units]	liquid phase oxygen concentration
C_{sensor}	[arbitrary units]	concentration indicated by oxygen sensor

f_s	[–]	fraction of solid particles due to solid skeleton structure, i.e., excluding pore volume
H_0	[m]	ungassed column height
H	[m]	dispersion height in the column
k_L	[m s^{-1}]	liquid-side mass transfer coefficient
k_{sensor}	[s^{-1}]	sensor time constant
U_G	[m s^{-1}]	superficial gas velocity

Greek symbols

ε_G	[–]	gas hold-up
ε_S	[–]	volume fraction of catalyst particles in gas-free slurry

Superscripts

*		refers to saturation condition

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