Study on Mass Transfer within the Microchannel Reactor

Dan Li

School of Chemical Engineering and Technology, Xi'an Shiyou University, Xi'an, China

hunter2011@foxmail.com

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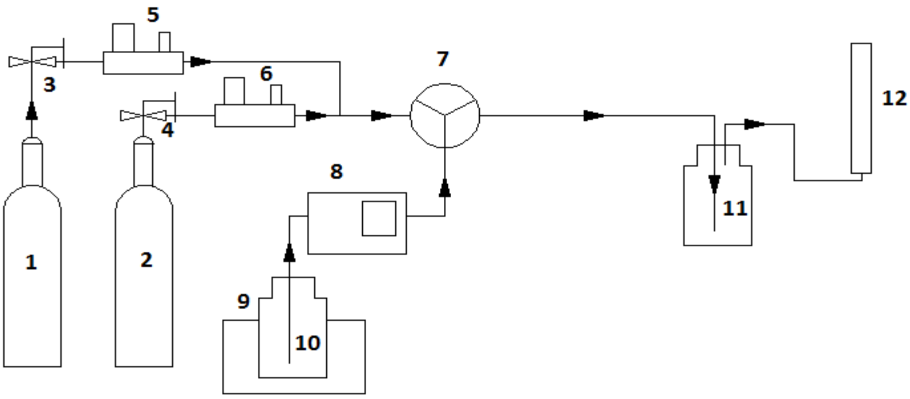
Abstract. Taking CO_2 absorption as background, this paper makes a research on the experiments of CO_2 absorption of the NaOH solution within microchannel reactor. By changing the concentration, superficial gas velocity and superficial liquid velocity of NaOH solution, their impact on the CO_2 absorption rate is studied, and the results show that the overall mass transfer coefficient $K_G a$ increases when NaOH solution concentration increases. Under the same superficial liquid velocity, when superficial gas velocity increases, $K_G a$ also increases, and with the increase of superficial gas velocity, the increasing trend gradually slows down. At the same superficial gas velocity, with the increase of superficial liquid velocity, $K_G a$ also increase, and with the increase of superficial gas velocity, the increasing trend becomes faster.

Experimental part

The experimental device is shown in figure 1, the ratio of N_2 and CO_2 gas flow is adjusted to 1: 1 by the mass flow meter, and the mixed gas gets into a microchannel of the microchannel reactor. The NaOH solution is withdrawn from advection pump at 30 ℃ super-heated water bath, then it flows into another microchannel of the microchannel reactor. Two-phase of liquid and gas contact in the main microchannel for the gas absorption process, and finally enter the gas-liquid separator for gas-liquid separation. The inner diameter of the microchannel reactor used in this experiment is 0.5mm. After the gas separation, the export flow is measured by the bubble flowmeter. Absorbing liquid titrates nitric acid solution to determine the amount of CO2 absorption. This experiment uses double indicator method, three consecutive parallel tests of each experiment are made to get the average.



1-N_2 cylinders 2-CO_2 cylinders 3, 4-Valve 5,6-Gas mass flow meter 7-Microchannel reactor 8-Advection pump 9-Water bath 10,11-Jars 12-Bubble flowmeter

Fig.1Schematic representation of the experimental setup.

Experimental principle

The parameters during liquid mass transfer process such as gas-liquid volumetric mass transfer coefficient, the phase boundary area usually uses chemical absorption method to measure. As to the different actual situation for devices, we can select specific gas liquid reaction systems to characterize [1, 2]. In order to increase the rate of mass transfer, this experiment adds NaOH into the water in order to increase the CO_2 absorption rate in N_2, and the reaction mechanism is as follows:

$$CO_2 + OH^- \rightarrow HCO_3^- \tag{1}$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \tag{2}$$

In the above two formulas, (1) is irreversible secondary reaction, (2) is proton transfer reaction, the reaction rate constant in (2) is much bigger than that in (1), so (1) is the rate controlling step. Under the experimental conditions, the solution is alkaline, the equilibrium concentration of HCO_3^- can be ignored, so combine (1) and (2), the reaction is as follows:

$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O \tag{3}$$

In this experimental system, the expression for the reaction rate equation is $r = k[CO_2][OH^-]$, k is the reaction rate constant in alkaline, and its value can be calculated by the correlations Pohorecki[3] put forward:

$$\log_{10} k = 11.916 - \frac{2382}{T} + \sum b_{ion} I_{ion} \tag{4}$$

Danckwert[4-7] developed that when alkali liquor absorbed CO_2, if $\sqrt{10^3 D_A k[OH^-]_0} \big/ k_L^0 >> 1 + C^* \big/ 10^3 [OH^-]_0$, quasi-order reaction occurs, and the liquid mass transfer coefficient can be predicted by the following equation:

$$(k_L a)^2 = 10^3 a^2 D_A k[OH^-]_0 + \frac{4a^2 D_A}{\pi T} \tag{5}$$

If $10^3 k[OH^-]_0 >> \frac{4}{\pi T}$, the above equation can be simplified to:

$$k_L a = a\sqrt{10^3 D_A k[OH^-]_0} \tag{6}$$

D_A is the diffusion coefficient of solute in solution, which can be calculated by the correlations Versteeg[8,9]put forward:

$$D_A = D_{w,A}(1 - 1.29 \times 10^{-4}[OH^-]) , \quad D_{w,A} = 2.35 \times 10^{-6} \exp(\frac{-2119}{T})$$

According to the relationship of gas phase total volume mass transfer coefficient, liquid volume mass transfer coefficient and gas volume mass transfer coefficient, the following equation can be obtained:

$$\frac{1}{K_G a} = \frac{H}{k_L a} + \frac{1}{k_G a} \tag{7}$$

Where, H is CO_2 solubility in water, which can be calculated by the correlations Weisenberger[8,10] put forward:

$$H = 10^{\sum h_i - h_G} \big/ H_w , \quad h_G = h_{G,0} + h_T (T - 298.15) , \quad H_w = 3.54 \times 10^{-7} \exp(2044 / T)$$

Substitute (6) into (7), we can get:

$$\frac{1}{K_G a} = \frac{1}{a} \frac{H}{\sqrt{10^3 D_A k\left[OH^-\right]_0}} + \frac{1}{k_G a} \tag{8}$$

$K_G a$ is total volume mass transfer coefficient, which is calculated by:

$$K_G a = \frac{L \Delta x}{(y_0 - y^*) PV} \tag{9}$$

Result and discussion

Effect of liquid phase NaOH concentration on gas overall mass transfer constant. Fig. 2 shows the trend of gas overall mass transfer coefficient with NaOH concentration in liquid absorption within the microchannel reactor. As can be seen, under different concentrations of NaOH solution, K_G is also different, and it increases with the increase of NaOH concentration. When the concentration of NaOH solution increases, the reaction rate will increase, thereby increasing the absorption rate. But with the increase of the NaOH solution concentration, the viscosity of the solution will increase correspondingly, which will make the diffusion coefficient of CO_2 in the solution decrease so as to increase the liquid mass transfer resistance [11]. According to the experimental results obtained, we can see that the promoting role in a chemical reaction is much greater than the mass transfer resistance the concentration increase brought. As Re_L increases, the liquid phase mass transfer coefficient and the phase boundary area also increase, thereby facilitating liquid transfer [11, 12]. Therefore, the Re_L increase has improved the capacity of gas-liquid two-phase mass transfer in microchannel reactor.

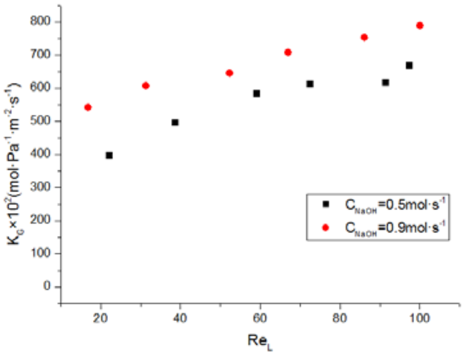


Fig.1.2 Effect of liquid phase NaOH concentration on K_G

Effect of superficial gas velocity on the overall mass transfer coefficient. Fig. 3 shows the effect of superficial gas velocity on overall mass transfer coefficient under different superficial liquid velocity when NaOH concentration is 0.5mol/L. As it can be seen from the figure, when superficial liquid velocity remains unchanged, with the increase of superficial gas velocity, $K_G a$ also increases. The mass transfer coefficient trend is basically the same with the phenomenon a number of researchers observed within the microchannel when the equivalent diameter is greater than 1mm [13-15]. It can also be seen from the figure that the increasing trend of $K_G a$ is gradually slowing down with the increase of superficial gas velocity. This is because when the superficial gas velocity increases, the gas-liquid two-phase flow pattern will change from bomb-like flow to dispersed flow, and the change in the flow pattern will gradually slow the increasing trend of overall mass transfer coefficient.

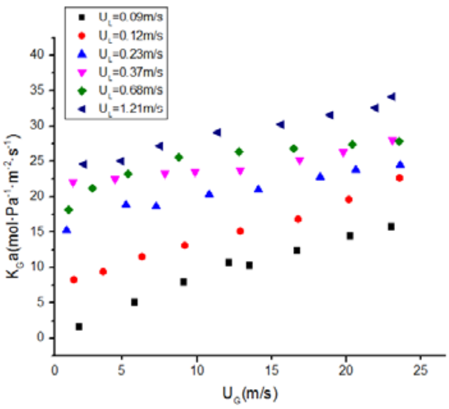


Fig. 3 Effect of superficial gas velocity on $K_G a$

Table 1 shows the mass transfer coefficient of the microchannel reactor and other conventional gas-liquid contactor the present study uses, which can be seen that the mass transfer coefficient of microchannel reactor is much bigger than that of traditional gas-liquid contactor. Microchannel has such a high mass transfer coefficient, which is particularly applicable for the multi-phase reaction whose controlling step is mass transfer [16]. Le Jun [17] used a microchannel reactor with rectangular cross section and equivalent diameter of 667μm, and he used 0.3mol·$L^{-1}$$NaHCO_3$/0.3

mol·L^{-1}NaCO$_3$ aqueous for absorption of CO2, with a total mass transfer coefficient of 21s^{-1}. Inoue [18] used H_2 and O_2 to make hydrogen peroxide in the micro-packed bed reactor with the overall mass transfer coefficient up to 3.8s^{-1}.

Table 1 the comparison of mass transfer coefficients in different gas-liquid contactors

Reactor Type	$k_L a \times 10^2$ (s^{-1})
Bubble tower	0.5-24
Packed tower, countercurrent	0.04-7
Packed column, stream	0.04-102
Spray tower	1.5-2.2
Couette Taylor stream reactor	3-21
Stirred tank	3-40
Spray absorber	2.5-122
Tubular reactor, vertical	2-100
Tubular reactors, horizontal and hovering	0.5-70
Static mixer	10-250
Gas-liquid microchannel contactor	30-2100
Microchannel in this experiment	40-3400

Effect of superficial liquid velocity on the overall mass transfer coefficient. Fig. 4 shows the effect of superficial liquid velocity on the overall mass transfer coefficient at different superficial gas velocity with NaOH concentration of 0.5mol/L. As can be seen from the figure, the trend is similar to that of the mass transfer coefficient shown in Figure 3. At any kind of superficial gas velocity, the overall mass transfer coefficient will increase when superficial liquid velocity increases, but the increase trend is faster. The reason for this phenomenon is that the flow pattern makes change. When the superficial liquid velocity increases, the gas-liquid two-phase interfacial area increases, and film thickness increases, and flow pattern becomes turbulent, so when superficial liquid velocity increases, the increase trend of overall mass transfer coefficient has not slowed.

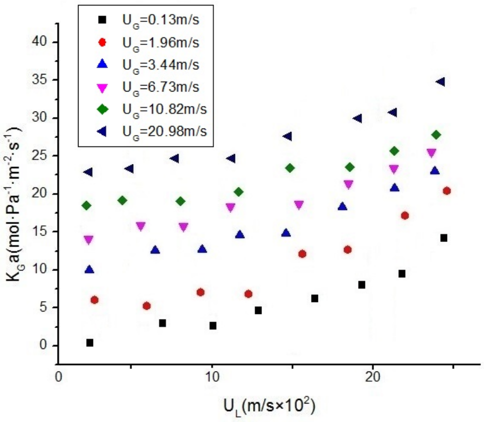


Fig. 4 Effect of superficial liquid velocity on $K_G a$

Summary

This paper examines the gas-liquid two-phase transfer characteristics in the circular microchannel with diameter of 0.5mm, which uses NaOH solution to absorb CO_2-N_2 mixture gas to measure the overall mass transfer coefficient, and then predict the gas-liquid two-phase mass transfer boundary area. The summary of this paper is as follows:

The gas overall mass transfer coefficient in microchannel reactor will increase when NaOH concentration increases, and the greater the gas phase is, the bigger the overall mass transfer coefficient is.

At the same superficial liquid velocity, the overall mass transfer coefficient also increases when superficial gas velocity increases, but the increase trend gradually slows down. This is because when the superficial gas velocity increases, the gas-liquid two-phase flow pattern will change from bomb-like flow to dispersed flow, and the degree reduction of film turbulence will cause the trend to slow down.

At the same superficial gas velocity, the overall mass transfer coefficient also increases when superficial liquid velocity increases, and the increase trend becomes faster with the increase of superficial gas velocity. This is because when the superficial liquid velocity increases, the gas-liquid two-phase flow pattern will not change basically, and the degree of film turbulence will be bigger and bigger.

Symbol Description

a ——Boundary area, m^2/m^3
b_{ion} ——Contribution of each ion in formula (4), m^3/mol
C^* ——Physical solubility of solute in the liquid phase, mol/m^3
D_A ——Solute diffusion coefficient in solution, m^2/s
$D_{w,\ A}$ ——Solute diffusion coefficient in water, m^2/s
h_G ——Gas properties constant, m^3/kmol
h_T ——Gas specific parameters of temperature effect, $m^3\cdot kmol^{-1}\cdot K^{-1}$
H ——Solubility of carbon dioxide in aqueous solution, $Pa\cdot m^3\cdot mol^{-1}$
H_w ——Solubility of carbon dioxide in water, $mol\cdot m^{-3}\cdot Pa^{-1}$
k ——Reaction rate constant in lye
$k_G a$ ——Gas film mass transfer coefficient, $mol\cdot Pa^{-1}\cdot s^{-1}\cdot m^{-3}$
$K_G a$ ——Overall mass transfer coefficient, $mol\cdot Pa^{-1}\cdot s^{-1}\cdot m^{-3}$
$k_L a$ ——Liquid film mass transfer coefficient, s^{-1}
L ——Liquid flow rate, $mol\cdot s^{-1}$
$[CO_2]$ ——Concentration of carbon dioxide in solution, $mol\cdot L^{-1}$
$[OH^-]_0$ ——Concentration of OH^{-1} in solution, $mol\cdot L^{-1}$
$[OH^-]$ ——Primary concentration of OH^{-1}, $mol\cdot L^{-1}$
P ——System pressure, Pa
T ——Temperature, K
V ——Microchannel volume, m^3
Δx ——Mole fraction changes of carbon dioxide in the liquid phase
y_0 ——Mole fraction of carbon dioxide in the gas phase body
y^* ——Balance mole fraction of carbon dioxide in the gas phase

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