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CHARACTERISTICS OF MASS TRANSFER BETWEEN GAS-LIQUID PHASES IN A HIGEE REACTOR

Article Highlights

- Reasonable assumptions of math method were introduced
- The diffusion-reaction mass transfer model predicted the absorption process in higee reactor well
- The dynamic mass transfer coefficient was appropriated to liquid lifetime

Abstract

In the absorption process of gas-liquid phases in rotating packed bed (RPB), the liquid flow on packing was assumed to be film-flow. Based on Higbie's penetration theory, the diffusion-reaction model in RPB was introduced to calculate the rate of gas absorption. Taking CO₂ (10%) + N₂ (90%) gas mixture and N-methyldiethanolamine (MDEA) aqueous solution as objects, the experiments of gas absorption were carried out at different gas flow rates, rotating speeds, temperatures, liquid flow rates and MDEA mass concentrations. The experimental data were compared with calculation results to found a good agreement in the rotating speed range of 400-1100 r/min. In this range, the rate of decarburization was in direct proportion to rotating speed, temperature and liquid flow rate, and inversely proportion to gas flow rate and MEDA mass concentration. The maximum deviation between experimental data and calculation results was 10%. Beyond the rotating speed of 1100 r/min, the rate of decarburization was dependent on the dynamic balance of gas-liquid system. In this area, the rate of decarburization was inversely proportion to rotating speed.

Keywords: lifetime of liquid film, concentration gradient, dynamic-state mass transfer, HiGee reactor.

The HiGee reactor is a new-type mixing and contact device, which has the characteristics of short residence time, homogeneous micromixing, and high mass-transfer coefficient. The gas-liquid mass transfer is intensified when the two phases contacting count-current in the packing. The height of mass transfer unit in RPB could be 1-2 order of magnitudes less than classical packed column [1-3].

Many researches have been done on the mass transfer process in higee reactor [4-10]. It was generally received that the huge effective mass transfer superficial area in higee reactor resulted in its high

mass transfer efficiency and the reactions accompanying the mass transfer were often taken as irreversible ones. Based on analysis of fluid flow velocity on the packing, reasonable assumptions and quantitative calculations on mass transfer, it was clarified that the high mass transfer efficiency of HiGee reactor was reflected in the high gas-liquid mass transfer coefficient. However, few studies of reversible reactions in HiGee reactors have been published. Thus, the gas-liquid mass transfer phenomena accompanied with reversible reaction in a HiGee reactor has been waiting to be discussed.

The reaction of liquid-film-controlled accompanied with reversible reaction was experimented in HiGee reactor. The different mechanisms for gas-liquid mass transfer under different flow conditions were discussed. On the strength of classical theories, the mathematic model was built to predict absorption

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performance and facilitation of mass transfer in higee reactor. The absorption of CO₂ by *N*-methyldiethanolamine (MDEA) was carried out in higee reactor. The mole fractions of CO₂ in the exit of HiGee reactor under different operation conditions were measured by gas chromatography. The experimental results showed the effective range of different model calculations.

EXPERIMENTAL

Figure 1 shows the schematic of the HiGee reactor. The packing was made of multi-layer stainless steel wire and had an inner diameter of 42 mm, outer diameter of 146 mm, and height of 20 mm. The stainless steel wire had a specific surface area of 500 m²/m³ and voidage of 97%. The aqueous MDEA was sprayed onto the inner edge of the HiGee reactor *via* a distributor. The liquid was passed through the packing by centrifugal force and collected by the enclosure of the HiGee reactor. The gas mixture consisted of 10% CO₂ and 90% N₂. The gas mixture was pushed from outer edge into the packing by gas pressure. The gas mixture was dissolved and reacted with MDEA while the gas and liquid contacted counter-currently in HiGee reactor. The extra gas was released to atmosphere. The amount of CO₂ in gas mixtures of entrance and exit were measured separately by gas chromatograph-mass spectrometer on line. The capacity of CO₂ in MEDA was tested by titration.

In the experiments, the gas flow range was 200–1100 L/h, the liquid flow range was 6–10 L/h, the liquid mass concentration range was 10–30%, the rotating speed range was 600–1300 r/min, and the operation temperature range was 293–313 K. In the HiGee reactor, aqueous MDEA was stroke and cut up by high-speed rotating packing. Since the interphase contact updated quickly, the lifetime of liquid film on the packing was short. The liquid film was replaced before CO₂ permeated completely into the liquid film. Owing to the gas-liquid system was far from steady mass transfer in liquid film, there was a high instantaneous concentration gradient on the new interphase. Therefore, the mass transfer was extremely intensified by the HiGee reactor.

Model development and solution

Model assumption

1) Most of the liquid contact and mass transfer with gas in film form. Previous studies have clarified that the liquid flow in HiGee reactor could be treated as laminar flow [11–13]. The average flow velocity of liquid film on the packing was about 0.2 m/s [13].

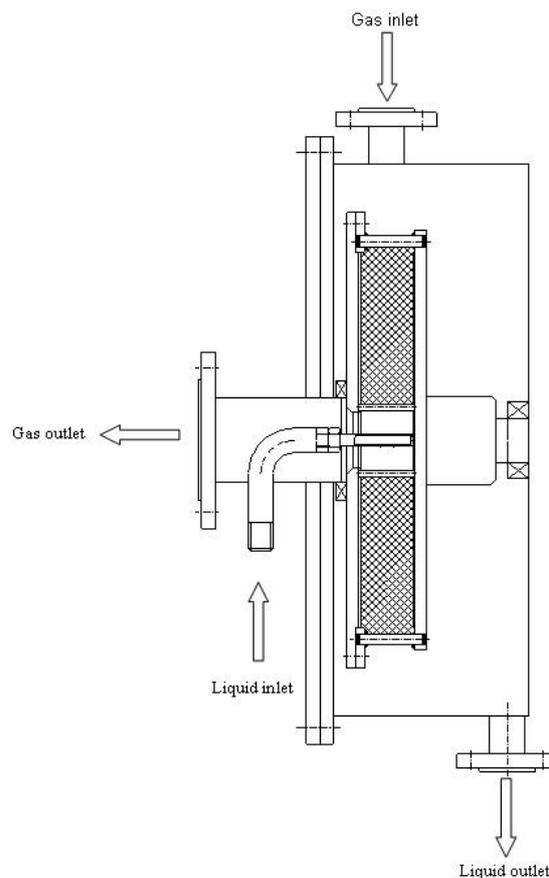


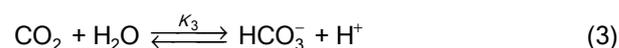
Figure 1. Schematic of higee reactor.

2) The packing surface is regarded as a gas-liquid mass transfer surface. The effective interfacial area equals to the packing surface area.

3) The packing is made of multi-layer stainless steel wire. Liquid film is renewed every time it passes through one layer. The mean lifetime of liquid film in each layer is constant. This constant is determined by liquid residence time and total number of packing layers.

Reaction mechanism

The process of CO₂ absorbed by MDEA consisted of several equilibrium reactions:



Only reactions (1), (3) and (5) affected the CO₂ absorption. Since the reaction rate of reaction (3) could be ignored [14], reactions (1) and (5) were treated as control steps of the absorption. Based on the literatures, reaction (1) was following the base catalysis mechanism [15], while reaction (5) was following the zwitterions mechanism [16].

The partial differential equations were built based on the Higbie penetration model to describe the diffusion and reaction mass transfer. All reactions in the mass transfer process were treated as reversible reactions. To be concise, the concrete modeling and solving process were referred to reference [17-20].

Enhancement factor and liquid mass transfer coefficient for absorption in HiGee reactor

In HiGee reactor, liquid film is renewed every time it passes through one layer. The refresh rate of liquid film was:

$$S = u \frac{N_2}{R_1 - R_2} \quad (7)$$

The mean radial flow rate on stainless steel wire was [21]:

$$u = 0.02107L^{0.2279}(\omega R)^{0.5448} \quad (8)$$

The mean lifetime of liquid film in packing was:

$$\bar{t} = \frac{1}{S} \quad (9)$$

Based on the percolation model, liquid mass transfer coefficient of CO₂ physical absorption was:

$$k_{L,CO_2}^0 = 2\sqrt{\frac{D_{CO_2}}{\pi\bar{t}}} \quad (10)$$

For the reaction of CO₂ absorbing by MDEA, the average mass transfer rate on each unit of phase interface area was:

$$\bar{N}_{CO_2} = \int_0^{\bar{t}} -D_{CO_2} \frac{\partial c_{CO_2}}{\partial x} \Big|_{x=0} \frac{1}{\bar{t}} dt \quad (11)$$

The enhancement factor of chemical absorption was:

$$E_{CO_2} = \frac{\bar{N}_{CO_2}}{k_{L,CO_2}^0 (c_{CO_2}^* - c_{CO_2}^0)} \quad (12)$$

The liquid mass transfer coefficient of CO₂ absorbing by MDEA in HiGee reactor was:

$$k_{L,CO_2} = E_{CO_2} k_{L,CO_2}^0 = \frac{\bar{N}_{CO_2}}{c_{CO_2}^* - c_{CO_2}^0} \quad (13)$$

Quantitative relation of mass transfer coefficient and liquid film lifetime

The thermodynamic mass transfer coefficient could be simulated in wetted wall column by two-film theory. The aqueous MDEA flow was gravity flow on wetted wall. Since the residence time of liquid film was longer than 1 s, a steady concentration gradient which independent on time could be built. The mass transfer coefficient was expressed as [14]:

$$k_L' = \sqrt{k_{OV} D_{CO_2}} \quad (14)$$

Combining the mass transfer model and Eq. (13), the dynamic mass transfer coefficient and its quantitative relation with liquid film period was achieved. Comparing the dynamic mass transfer coefficient with thermodynamic mass transfer coefficient, it was found that these two numbers agreed when the liquid film period greater than 0.6 s.

Figure 2 shows the concentrations of CO₂ and MDEA at the interface with penetrating depth at different liquid film lifetimes. The CO₂ concentration at the interface decreased with increasing penetrating depth, while the MDEA concentration showed the opposite behavior.

Before the steady concentration gradient was built, liquid film was cut up by stainless steel wire packing. For CO₂, the depth of penetration was shallow and the concentration distribution was steep. The mass transfer process was tremendously intensified. In the experimental HiGee reactor, at a temperature of 293.15 K and packing rotating speed of 1100 rounds/s, the liquid film lifetime was 0.014 s and the depth of penetration was 2×10^{-5} m.

Radial material balances in HiGee reactor

The radial equilibrium concentration of CO₂ could be deduced by Eqs. (2) and (3):

$$c_{CO_2,eq} = \frac{1}{K_2 K_3} \frac{(c_{R_3N,total} - c_{R_3N}) c_{HCO_3^-}}{c_{R_3N}} \quad (15)$$

Material balance of CO₂ was calculated in the infinitesimal with radius of r , length of dr , and height of h :

$$k_y \alpha \left[y - \frac{H_{CO_2}}{P} \frac{1}{K_2 K_3} \frac{(c_{R_3N,total} - c_{R_3N}) c_{HCO_3^-}}{c_{R_3N}} \right] \times 2\pi r h R dR = G_{N_2} d \left(\frac{y}{1-y} \right) \quad (16)$$

The component material balance of HCO₃⁻ and R₃N were:

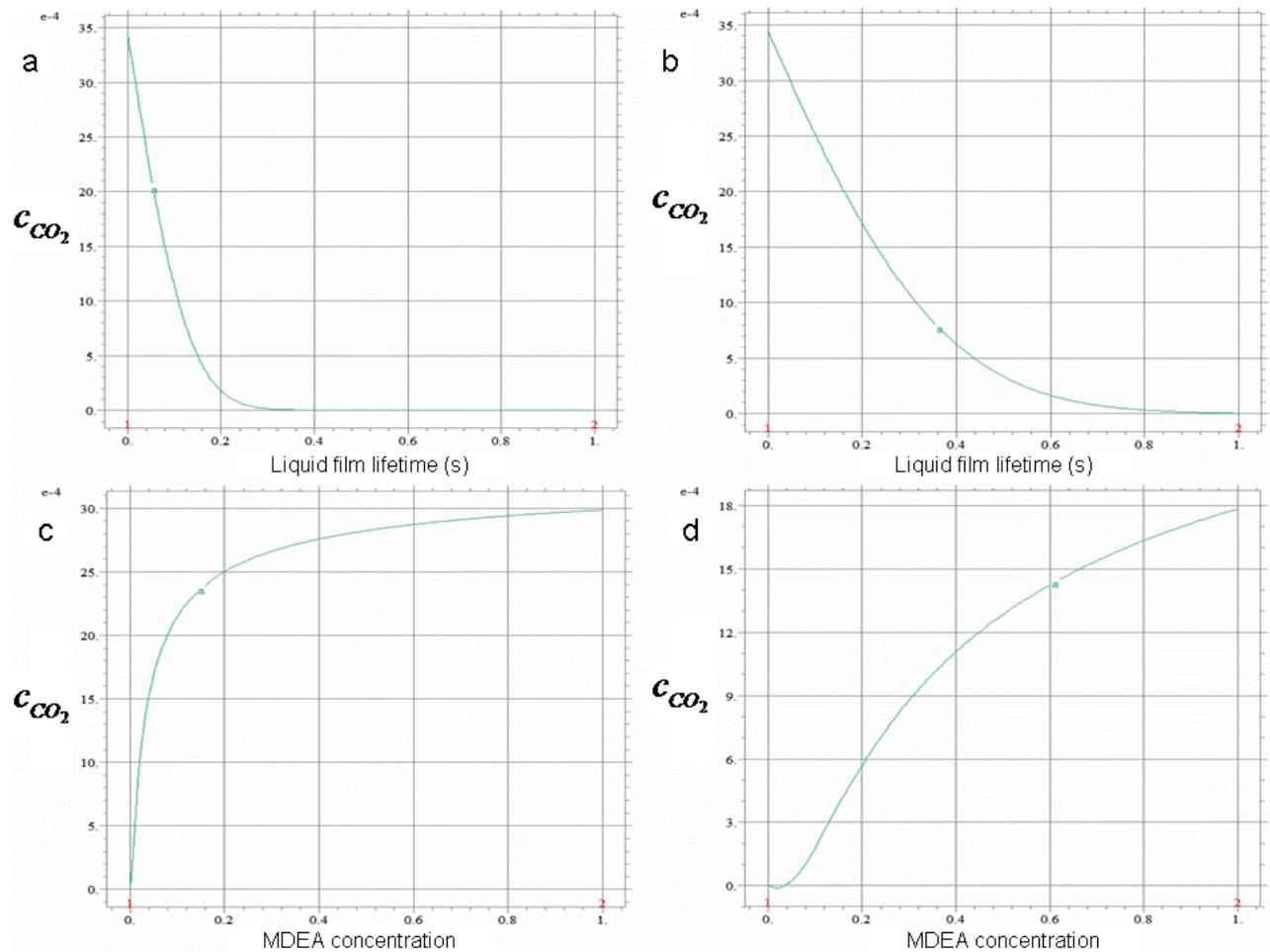


Figure 2. CO₂ concentration at interface variations with liquid film lifetime and MDEA concentration: a) 10% MDEA; b) 50% MDEA; c) 0.1 s liquid film lifetime; d) 0.6 s liquid film lifetime.

$$k_L \alpha \frac{P}{H_{CO_2}} \times \left[y - \frac{H_{CO_2}}{P} \frac{1}{K_2 K_3} \frac{(c_{R_3N, total} - c_{R_3N}) c_{HCO_3^-}}{c_{R_3N}} \right] \times 2\pi h R d R = Q d c_{HCO_3^-} \quad (17)$$

$$-k_L \alpha \frac{P}{H_{CO_2}} \times \left[y - \frac{H_{CO_2}}{P} \frac{1}{K_2 K_3} \frac{(c_{R_3N, total} - c_{R_3N}) c_{HCO_3^-}}{c_{R_3N}} \right] \times 2\pi h R d R = Q d c_{R_3N} \quad (18)$$

where $k_y = 0.082 T k_L P / H$.

The liquid flow rate was treated as constant in calculation. Simultaneous differential Eqs. (16)-(18) were solved by the Runge-Kutta method to gain the radial CO₂ concentration distribution on packing.

RESULT AND DISCUSSION

The CO₂ absorption by MDEA was carried out at different experimental conditions and the data were gained by measured by gas chromatograph-mass spectrometer. The investigation factors included gas flow rate, rotating speed, temperature, liquid flow rate, and MDEA mass concentration. All experimental data were compared with model simulation. To distinguish them, the experimental data were expressed in point form and the model simulations were expressed in line form in all the figures in later work.

To express the degree of decarburization more directly, the rate of decarburization was introduced as:

$$\Delta y = 1 - \frac{y_{out}}{y_{in}} \quad (19)$$

In the model assumption, the process of CO₂ absorption by MDEA was described as liquid-film-control. Keep the MDEA concentration of 10%, the

temperature of 293 K, and the liquid flow rate of 6 L/h. To verify the theory, experiments were carried out in a wide gas flow range. The experimental results and calculations are compared in Figure 3.

It can be observed from Figure 3 that the experimental results and calculation data agreed well at different rotating speed. The rate of decarburization decreased with the gas flow rate increasing. Since the liquid film lifetime decreased with rotating speed increasing, the absorption effect was better at high rotating speed. The model calculation fit the experimental data well in a wide gas flow rate range. The experimental results verified that the CO₂ absorption in this research was liquid-film-control, and the model assumption was reasonable. Due to inevitable imperfection in experiments, all experimental data were below the calculation results. It also could be seen in Figure 3, at gas flow rates higher than 800 L/h, the rate of decarburization approached a constant value at all experimental conditions. To investigate the effect factors in the absorption process, the gas flow rate was set at 1100 L/h in later experiments.

In the previous model, the rate of decarburization was in direct proportional to liquid flow rate. The experiments were carried out at temperature of 293 K and liquid flow rate of 6 L/h under three MEDA

concentrations to test the model calculation at different rotating speeds. The experimental results are shown in Figure 4.

The calculation curve in Figure 4 shows the rate of decarburization is in direct proportion to rotating speed. However, the experimental data shows different variation trend. The rate of decarburization grows with rotating speed under 1100 rpm. In this rotating speed range, the experimental data agree with calculation results. When the rotating speed is higher than 1100 rpm, the rate of decarburization is inversely proportional to the rotating speed. The experimental results indicate that the previous model is appropriate in the rotating speed range of $\omega < 1100$ rpm.

Physical absorption plays an important role in the experimental process. At high rotating speed, the liquid turbulence was strengthened. According to the literature [22], high turbulent degree was adverse to physical absorption limitation.

Experiments under different rotating speed clarified that the obverse model has not considered the end effect area and the cavity area in RPB. When the rotating speed $\omega < 1100$ rpm, the CO₂ absorption in end effect area and cavity area did not reach the dynamic equilibrium [22]. In this condition, the rate of decarburization only related to the refresh rate of

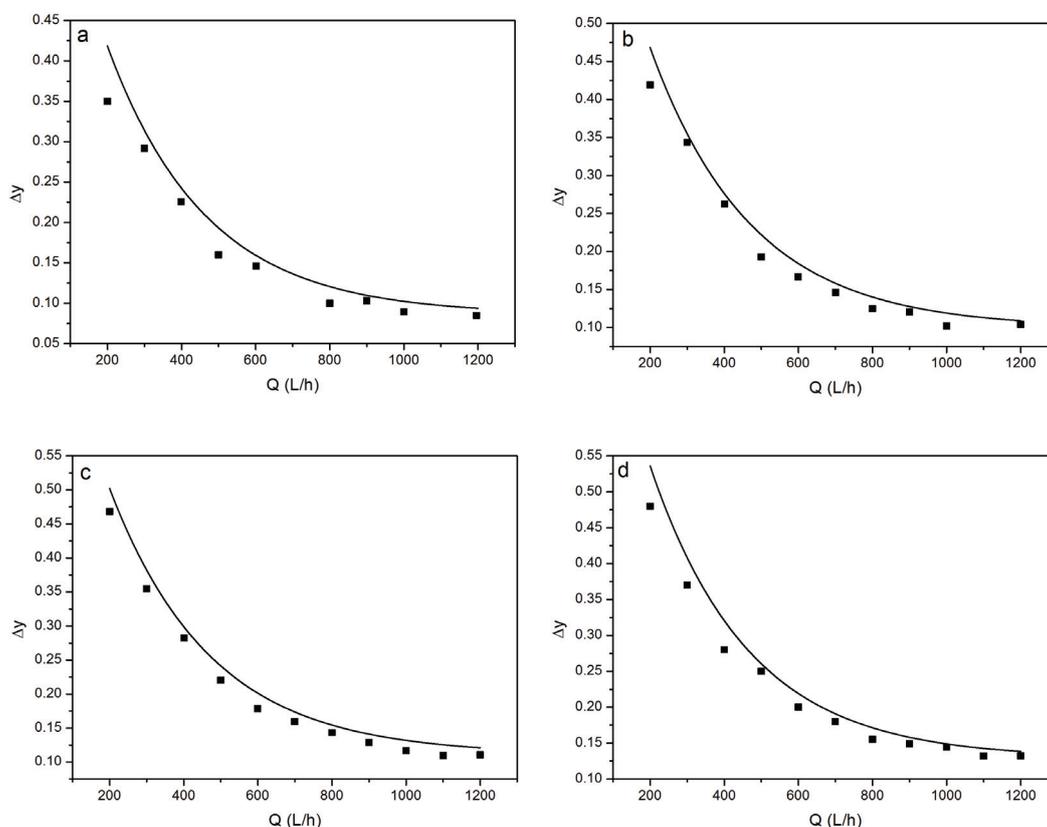


Figure 3. Rate of decarburization deviations with gas flow rate: a) 500; b) 700; c) 900; d) 1100 rpm.

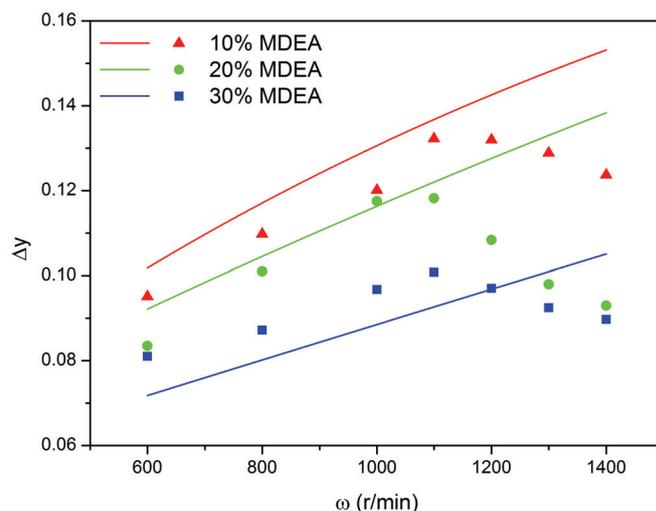


Figure 4. Rate of decarburization deviations with rotating speed at different MDEA concentrations.

liquid film which depended on packing type, liquid flow rate and rotating speed. As a result, the model calculation fit the experimental data well at the rotating speed range of 600–1100 rpm. At the inflection point of experimental curve the rotating speed was 1100 rpm. In other words, the absorption process approached to its limitation in end effect area and cavity area after rotating speed of 1100 rpm. The calculation method was probable only at rotating speeds before the inflection point. In this way, the following experiments were all carried out at the rotating speed of 1100 rpm.

Keeping the MDEA concentration of 10%, the experiments were taken at different liquid flow rates and temperatures. The experimental results are given in Figure 5.

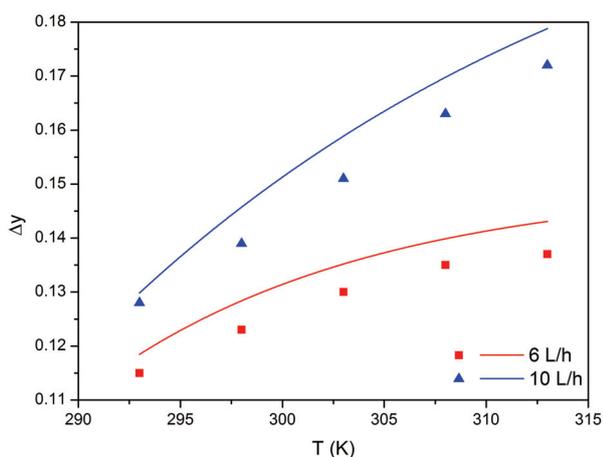


Figure 5. Rate of decarburization deviations with temperature at different liquid flow rate.

Figure 5 shows that the calculation agrees with experimental result. However, the rate of decar-

burization is more sensitive to temperature than liquid flow rate.

Due to the reaction mechanism, low concentration of MEDA was benefit for the target absorption. At the constant gas flow rate of 1100 L/h and rotating speed of 1100 rpm, the experimental temperature was set as 303 K and liquid flow rate as 6 L/h to investigate the effect of MDEA concentration. The experimental data are given in Figure 6.

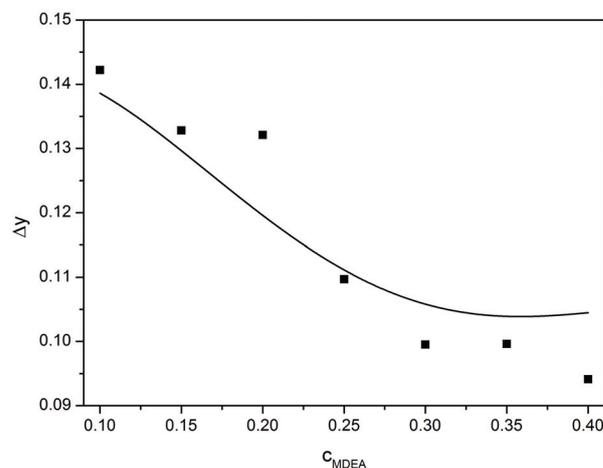


Figure 6. Rate of decarburization deviations with MDEA concentration.

It can be seen in Figure 6 that the rate of decarburization decreases with the MDEA concentration increasing. When the mass concentration of MEDA is larger than 30%, the rate of decarburization goes approach to a constant. Over-high concentration of MDEA is not available for the CO₂ absorption in the RPB.

CONCLUSIONS

1) Through quantitative comparison of thermodynamic and dynamic mass transfer coefficient, the assumptions of math method were indicated to be reasonable. The mass transfer coefficient was magnified in the HiGee reactor. The dynamic mass transfer coefficient was inversely proportional to liquid film lifetime.

2) The diffusion-reaction mass transfer model in this article was feasible for investigating the gas-liquid mass transfer accompanied with reversible reaction in a HiGee reactor at specific range of rotating speed. The math method predicted the absorption performance of the hige reactor well.

Acknowledgement

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Nomenclature

D	diffusion coefficient, m^2/s
G_{N_2}	volume flow rate, m^3/s
H	Henry's coefficient, $Pa/(m^3 \cdot mol)$
h	height of packing, m
K	equilibrium constant
k_L	liquid mass transfer coefficient, m/s
k_{OH^-}	CO_2 hydration reaction rate constant, $m^3/(kmol \cdot s)$
k_{OV}	total constant of pseudo-first-order reaction rate, s^{-1}
$k_{2,MDEA}$	second order reaction rate constant, $m^3/(kmol \cdot s)$
L	liquid flux, m/s
\bar{N}_{CO_2}	mean mass transfer rate of CO_2 on unit interfacial area, $kmol/(m^2 \cdot s)$
P_{CO_2}	partial pressure of CO_2 in gas, kPa
Q	liquid volume flux, m^3/s
R	geometric mean radius, m
r	reaction rate, $kmol/(m^3 \cdot s)$
T	temperature, K
\bar{t}	mean liquid film lifetime, s
y_{CO_2}	mole fraction of CO_2
Δy	rate of decarburization
α	specific surface area, m^2/m^3
ω	rotating speed, rpm

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NAUČNI RAD

KARAKTERISTIKE PRENOSA MASE IZMEĐU GASNE I TEČNE FAZE U HIGEE REAKTORU

U procesu apsorpcije gasne u tečnu fazu u rotirajućem pakovanom sloju (RPS), pretpostavljeno je da je strujanje tečnosti preko pakovanja filmsko strujanje. Zasovan na Higbijevoj penetracionoj teoriji, difuziono-reakcioni model je korišćen za RPS da bi se izračunala brzina apsorpcije gasa. Apsorpcija gasa u sistemu gasne smeše CO₂ (10%) i azota (90%) i vodenog rastvora N-metildietanolamina (MDEA) proučavana je pri različitim protocima gasa, brzinama obrtanja, temperature, protocima tečnosti i koncentracijama MDEA. Poređenje eksperimentalnih i izračunatih rezultata je pokazalo dobro slaganje u opsegu brzine obrtanja 400 do 1100 min⁻¹. U ovom opsegu, brzina razugljeničenja je bila direktno proporcionalna brzini obrtanja, temperaturi i protoku tečnosti, a obrnuto proporcionalna protoku gasa i koncentraciji MDEA. Maksimalno odstupanje između eksperimentalnih i izračunatih rezultata je bilo 10%. Pri većim brzinama od 1100 min⁻¹ brzina razugljeničenja je zavisila od dinamičke ravnoteže sistema gas-tečnost. U ovoj oblasti je brzina razugljeničenja bila obrnuto proporcionalna brzini obrtanja.

Ključne reči: životni vek tečnog filma, gradijent koncentracije, prenos mase u dinamičkom stanju, HiGee reaktor.