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A novel rate of the reaction between NaOH with CO_2 at low temperature in spray dryer

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ABSTRACT

Carbon dioxide (CO_2) is an influential greenhouse gas that has a significant impact on global warming partly. Nowadays, many techniques are available to control and remove CO_2 in different chemical processes. Since the spray dryer has high removal efficiency rate, a laboratory-scale spray dryer is used to absorb carbon dioxide from air in aqueous solution of NaOH. In the present study, the impact of NaOH concentration, operating temperature and nozzle diameter on removal efficiency of CO_2 is explored through experimental study. Moreover, the reaction kinetic of NaOH with CO_2 is studied over the temperature range of 50–100 °C in a laboratory-scale spray dryer absorber. In the present contribution, a simple reaction rate equation is proposed that shows the lowest deviation from the experimental data with error less than 2%.

1. Introduction

It is well known that CO_2 plays a dominating role in the greenhouse gases [1–7]. Global climate change leads to the high interest in the technologies relevant to the CO_2 capturing that is one of the potential methods to reduce greenhouse gas emissions [8–12]. Many alternative strategies are proposed to reduce the emission of CO_2. Among them, reactive absorption as an economically feasible method has been extensively studied for CO_2 capturing [8].

Spray dryer is a chamber in which the liquid solution is sprayed by atomizer as droplets into hot flow gas, resulting in drying the liquid droplets. In spray drying system, the moisture on the droplets is evaporated gradually, while the absorbents in the droplets react with impurities, simultaneously. Spray dryer is a well-known process in industry, e.g. for the production of ceramic precursors, and temperature-sensitive pharmaceuticals. This device has no wastewater products and can control CO_2 emission into atmosphere. The performance of spray drying was improved and high removal efficiency rates were obtained for this device [10,13–16]. These researches only have used spray dryer as a simple device and no data regarding its performance on reactive absorption have been reported. Up to now, only a semi-empirical kinetic model has been proposed in Ref. [16] for a spray-dryer setup over the temperature range of 100–200 °C. It has been found that when the operating temperature highly increases, the removal efficiency of CO_2 decreases. Therefore, it seems that exploring a new reaction rate between CO_2 and NaOH at low temperatures can be helpful for increasing the removal efficiency of CO_2. In fact, the description and prediction of the reaction kinetics in reactive systems, under given process conditions, is still a serious weakness in the modeling of processes including CO_2 capturing. The lack of existing literature in reactive absorption in spray dryer motivates the authors to study this process in more details. Accordingly, such study is undertaken and a new rate equation is proposed for low temperatures CO_2 removal in spray dryer device. Furthermore, effect of absorbent concentration, operating temperature and nozzle diameter on removal efficiency of CO_2 is investigated.

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2. Experiments

Commercial CO_2 gas with 99% purity and pellets of sodium hydroxide that were purchased from the Ruham gas Company (50 kg) and the Kimiaexir Company in Iran, respectively, are used. The required air for the study is supplied by a laboratory scale compressor. The NaOH pellets are dissolved in distilled water and continuously fed into spray dryer by pump. A schematic diagram of the experimental apparatus is shown in Fig. 1. In this setup, flow rate of air is monitored by a velocity meter and the flow of CO_2 is adjusted with a rotameter (to avoid solidification, an internal heater is used for CO_2 cylinder). The mixture of air and CO_2 is preheated by an electronic heater and fed into the spray dryer from the top. The feed stream (aqueous solution of NaOH) is concurrently fed to the drying chamber. The CO_2 concentrations at the inlet and outlet of spray dryer are measured by an infrared CO_2 gas monitor (0–3000 ppm and 0–100% in volume; ±2% uncertainty Edinburgh Instruments Ltd). Typically, the gas mixture (air and CO_2) is heated to 50–100 °C and this stream sprayed 3 wt % of aqueous NaOH into the reaction chamber of spray dryer (0.25 m × 0.45 m). In this process, heat and mass transfer and the chemical reaction occur in the reactive spray dryer, simultaneously. Generally the process includes:

1 Mass transfer of CO_2 from the gas stream to the droplet surface.
2 Absorption of CO_2 at the droplet surface, dissolution of CO_2 in the droplet and dissociation:

$$CO_2\ (gas) \rightarrow CO_2\ (aq) \tag{1}$$

$$CO_2\ (aq) + H_2O\ (liq) \leftrightarrow H_2CO_3 (liq) \tag{2}$$

$$H_2CO_3\ (liq) \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+ \tag{3}$$

3 Chemical reaction between dissolved CO_2 and the dissolved CO_2 reagent:

i- Dissolution of sorbent:

$$NaOH\ (s) \leftrightarrow NaOH\ (aq) \leftrightarrow Na^+ + OH^- \tag{4}$$

ii- Precipitation of sodium carbonate:

$$CO_3^{2-} + 2Na^+ \leftrightarrow Na_2CO_3(s) \tag{5}$$

4 Evaporation of the water in the droplet.

Generally, the overall chemical reaction can be written in a simple form as:

$$CO_2 + 2NaOH \leftrightarrow Na_2CO_3 + H_2O \tag{6}$$

Each experiment is carried out for 10 min by considering the liquid/gas weight ratio less than 0.2 to prevent weeping and also to reach the complete drying. Hence, no weeping is found during experiments. It is interesting to note that due to solid formation during the reaction, washing the dryer chamber and nozzle is crucial. In order to run a new experiment, the dryer chamber is washed by distilled water for 1 h, while no CO_2 and NaOH present in feed streams. Afterwards, the pump is turn down and dryer chamber is dried by clean air for 30 min at 150 °C. When no liquid is seen in the chamber, clean air and CO_2 are mixed together and fed to the dryer. After the temperature in the spray dryer reached to 50–100 °C range and the inlet concentration of CO_2 became stable, the absorbent is sprayed into the dryer chamber. In order to explore the absorption performance, removal efficiency (η) is used. Removal efficiency defines the percentage of removed CO_2 during absorption operation [17,18]. The removal efficiency for CO_2 is simply determined from the difference between the amounts of CO_2 entering and leaving the dryer chamber as follows

$$E(\%) = \frac{Y_{in} - Y_{out}}{Y_{in}} \tag{7}$$

It is worth mentioning that all experiments were conducted at summer of 2013 from 7 to 11 a.m., accordingly, a constant value for relative humidity of clean air is assumed during all experiments.

3. Results and discussions

3.1. Absorption performance

The removal efficiency of CO_2 as a function of operating temperature is shown in Fig. 2 with the inlet CO_2 concentration

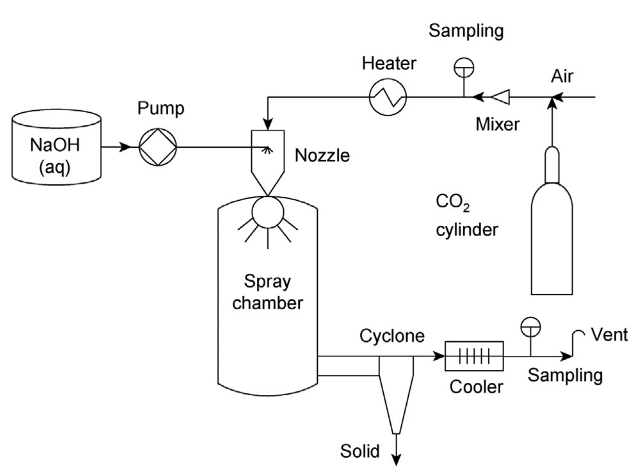

Fig. 1. Spray dryer setup.

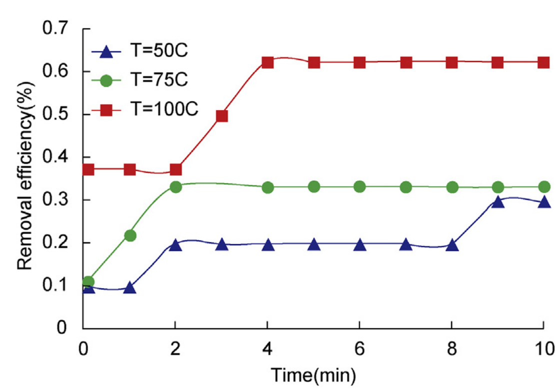

Fig. 2. Effect of operating temperature on absorption performance.

of 4%. As observed in the figure, with increasing the operating temperature, the reaction rate increases resulting in enhancement of the CO_2 removal efficiency. Fig. 2 shows that the maximum removal efficiency of 63% is related to 100 °C with 3 wt % of aqueous NaOH for the rate of 0.063 lit/s. Moreover, the sharp change in the green line shown in Fig. 2 returns to the accuracy of the CO_2 analyzer as well as higher reaction rate. In order to evaluate the influence of the absorbent concentration, two different aqueous solution of NaOH with the values of 3 and 1 wt % is used and the results are depicted in Fig. 3. As can be seen, increasing the absorbent concentration from 1 to 3 wt % leads to an enhancement in removal efficiency due to providing higher driving force to the reaction. As the concentration of absorbent is increased, the rate of reaction will also be favored due to providing higher concentration of the reactant.

Moreover, the effect of nozzle diameter is examined using the nozzle diameters of 0.5 mm and 1 mm. As shown in Fig. 4, with an increase in the nozzle diameter, the removal efficiency at 100 °C for 3 wt % solution of NaOH reduces due to the smaller surface area of droplets. Consequently, the smaller nozzle diameter provides a better performance for spray drying process.

3.2. Kinetic rate equation

To develop a kinetic rate equation over a low range of temperature, the absorption performance is measured for three different temperatures of 50, 75 and 100 °C. The experimental conditions used in the present study for absorbents concentration, the absorbent inlet rate and the nozzle diameter are kept constant with the values of 3 wt %, 0.063 lit/s and 5 mm, respectively. Based on differential analysis, a rate equation is considered for CO_2 capturing in a lab-scale spray dryer and the kinetics parameters are calculated by fitting experimental data to a kinetic model by using a multivariable nonlinear regression method to minimize the sum of the square of residuals. In nonlinear regression method, the dependent variables are regressed and modeled as a non-linear function of independent variables. To achieve this goal, the nonlinear regression toolbox of polymath software is used. In authors' previous work, polymath software was also used to predict kinetic constants in methanol dehydration process [19].

Based on the Lee [20] study, the molar rate of CO_2 removal by the NaOH can be described by Eq. (8)

$$-r_{CO_2} = \frac{1}{M_{NaOH}}\left(\frac{dy}{dt}\right) \rightarrow -r_{CO_2} \times M_{NaOH} = -R_{CO_2} = \left(\frac{dy}{dt}\right) \tag{8}$$

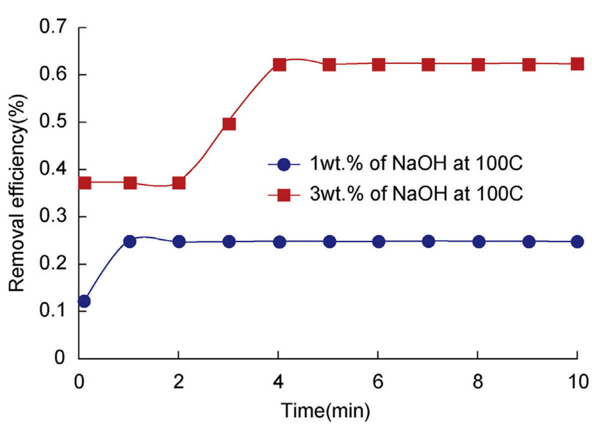

Fig. 3. Effect of absorbent concentration on absorption performance.

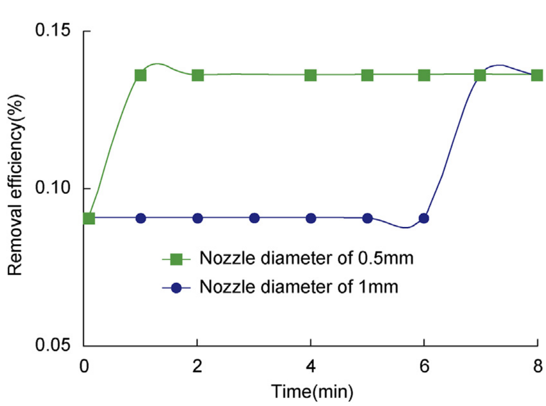

Fig. 4. Effect of nozzle diameter on absorption performance.

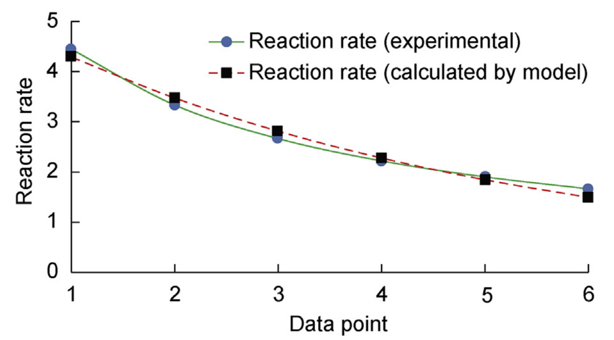

Fig. 5. A comparison between experimental and calculated reaction rates at 50 °C.

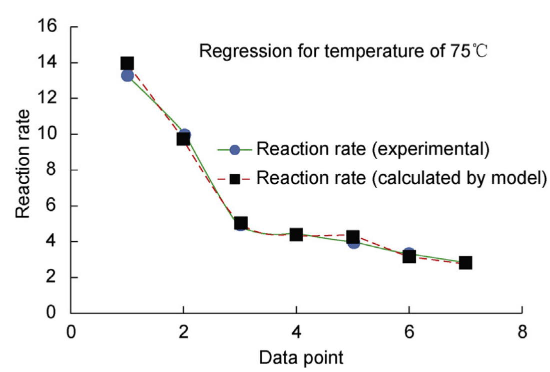

Fig. 6. A comparison between experimental and calculated reaction rates at 75 °C.

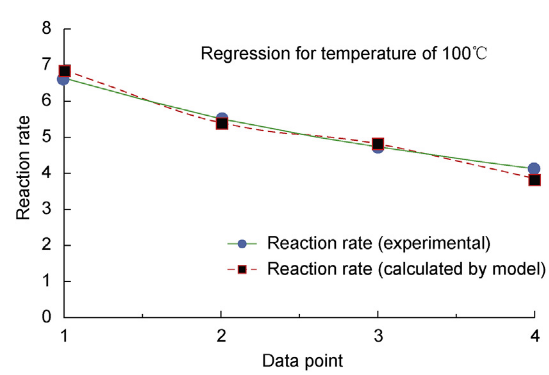

Fig. 7. A comparison between experimental and calculated reaction rates at 100 °C.

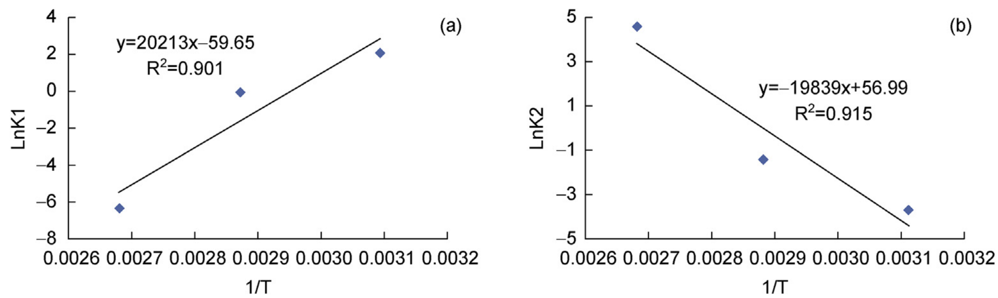

Fig. 8. The kinetic parameters of (a) K1 and (b) K2.

where r_{CO2} is the molar rate of CO_2 removal per unit mass of NaOH, and M_{NaOH} is the molecular weight of NaOH. First the change of CO_2 mole fraction (dy) versus time (dt) is plotted. After fitting a smooth curve to the available points, slope at each point is calculated. Each slope equals to the reaction rate multiplied by the NaOH molecular weight ($-r_{CO_2} \times M_{NaOH}$) at that special point. Figs. 5–7 indicate a well agreement between experimental and calculated reaction rates using Eq. (8) and Eq. (9) at 50 °C 75 and 100 °C, respectively. The temperature dependencies of the kinetic parameters are also determined by assuming the Arrhenius equation with R^2 of 0.91 as given in Fig. 8. The obtained rate expression is as follows:

$$-r_{CO_2} \times M_{NaOH} = -R_{CO_2} = K1 \times \frac{\exp(-K1 \times K2 \times t)}{1} \quad (9)$$

$$K1 = A_1 \exp\left(-\frac{E_1}{RT}\right) = 1 \times 10^{-26} \exp\left(\frac{4201}{RT}\right) \quad (10)$$

$$K2 = A_2 \exp\left(-\frac{E_2}{RT}\right) = 6 \times 10^{24} \exp\left(-\frac{4123}{RT}\right) \quad (11)$$

In order to find K1 and K2, 17 data points are used, in this study. It should be noted that the information about the values of E_1 and E_2 is not found in the literature, while present study shows that the calculated average values of E_1 and E_2 are −4.2 and + 4.1 kJ/mol, respectively. By considering a good agreement between the experimental results and calculated data by the kinetic with an error less than 0.02%, it is deduced that the proposed model satisfactorily simulates the experimental data and it is reliable enough for mathematical modeling and data prediction.

4. Conclusion and final remarks

In this study, effect of NaOH concentration, operating temperature and nozzle diameter on removal efficiency of CO_2 in spray dryer including aqueous solution of NaOH was studied. It was observed that the CO_2 removal efficiency directly increases with increasing the operating temperature. Increase of the NaOH concentration from 1 to 3 wt % leads to an enhancement in CO_2 removal efficiency due to providing higher concentration of the reactant. In addition, an increase in the nozzle diameter from 0.5 to 1 mm showed a decreasing trend for removal efficiency due to smaller surface area of the droplets.

A new reaction rate was proposed for CO_2 capturing in aqueous solution of NaOH using a multivariable nonlinear regression method. Comparison of the experimental results and calculated data by the kinetic model revealed a good agreement between the results with an error less than 0.02. In order to improve the rate of the reaction, considering the effects of gas inlet rate, relative humidity of air, absorbent inlet rate and mixture of absorbents into the model is suggested for future works.

Nomenclature

A1	Parameter of K1 (mol/s)
A1	Parameter of K2 (mol/s)
aq	Aqueous solution
E1 and E2	Activation Energy (kJ/mol)
K1 and K2	Kinetic parameters (mol/s)
liq	Liquid
M_{NaOH}	Molecular weight of NaOH (g/mol)
$-r_{CO2}$	Molar reaction rate of carbon dioxide per gram of solid (mol/g/s)
R	Universal gas constant
s	Solid
t	Time (s)
T	Temperature (K)
Y_{in}	Mole fraction of carbon dioxide entering the dryer
Y_{out}	Mole fraction of carbon dioxide leaving the dryer
η	Removal Efficiency

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