Simultaneous Online Measurement of H₂O and CO₂ in the Humid CO₂ Adsorption/Desorption Process

Qingni YU,^{*,**} Sha YE,^{*} Jingke ZHU,^{*} Lecheng LEI,^{*} and Bin YANG^{*†}

^{*}Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, P. R. China

^{**}China Astronaut Research and Training Center, Beijing 100094, P. R. China

A dew point meter (DP) and an infrared (IR) CO₂ analyzer were assembled in a humid CO₂ adsorption/desorption system in series for simultaneous online measurements of H₂O and CO₂, respectively. The humidifier, by using surface-flushing on a saturated brine solution was self-made for the generation of humid air flow. It was found that by this method it became relatively easy to obtain a low H₂O content in air flow and that its fluctuation could be reduced compared to the bubbling method. Water calibration for the DP-IR detector is necessary to be conducted for minimizing the measurement error of H₂O. It demonstrated that the relative error (RA) for simultaneous online measurements H₂O and CO₂ in the desorption process is lower than 0.1%. The high RA in the adsorption of H₂O is attributed to H₂O adsorption on the transfer pipe and amplification of the measurement error. The high accuracy of simultaneous online measurements of H₂O and CO₂ is promising for investigating their co-adsorption/desorption behaviors, especially for direct CO₂ capture from ambient air.

Keywords CO₂ capture, water calibration, co-adsorption, humidifier, dew point meter, infrared CO₂ analyzer

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Introduction

It is well known that anthropogenic CO₂ emissions are major contributors to climate change. The ever-increasing concentration of atmospheric CO₂, from 278 ppm to more than 390 ppm today is derived from increasing fuel consumption after the industrial revolution. Capturing CO₂ directly from ambient air, commonly referred to as direct air capture (DAC),^{1,2} can be used for CO₂ stabilization in the atmosphere. CO₂ removal is also conducted in the life-support systems (LSS) when CO₂ reaches a relatively high concentration, such as in submarines and space capsules, which would threaten the survival of humans in the enclosed spaces.³⁻⁶ An adsorption technology has been proven to be one of the most efficient ways for CO₂ capture or removal, because high-purity streams can be obtained with low energy consumption.⁷⁻⁹ Generally, the H₂O content is high in the DAC process and LSS due to the moist air.^{10,11} Therefore, it is crucial to accurately measure the H₂O and CO₂ concentrations in order to conduct investigations of their corresponding adsorption behaviors, especially in the online way. An infrared CO₂ analyzer,^{12,13} gas chromatography (GC)^{13,14} and a gas chromatography-mass spectrometer (GC-MS)¹⁵ were common for online measurements of CO₂. However, they failed to achieve H₂O and CO₂ elution curves simultaneously in the humid CO₂ co-adsorption/desorption process. In addition, thermogravimetric analysis (TGA)¹⁶⁻¹⁹ and TGA-MS²⁰⁻²² were

also used to study CO₂ adsorbent/desorption, which can provide a quantitative understanding of CO₂ uptake in the adsorption of dry CO₂. However, it is hard to collect the individual concentrations of H₂O and CO₂ in the co-adsorption/desorption process because the response of TGA is a result of the overall weight gain or loss. In particular, the adsorption behavior in the pan obtained from TGA was significantly different from that in adsorption-column reactors. Serna-Guerrero and coworker installed MS to the outlet of a fixed-bed reactor for collecting CO₂ and H₂O breakthrough data and their elution curves.²³ The concentrations of CO₂ and H₂O were determined using a single ion monitor (SIM) with $m/z = 44$ and $m/z = 18$, respectively. Since the gas flow rate in the practical reactor is much higher than that required by MS, the gas flow must be split before entering MS, which would result in measurement errors. In addition, MS is relatively expensive, and it would be easily contaminated if used as an online monitor.

The combination of the humidity sensor with the infrared (IR) CO₂ analyzer in series was a simple and practical way to obtain breakthrough and elution curves of CO₂ and H₂O simultaneously.^{13,24} However, the concentration difference between the real H₂O and the measured H₂O was up to 17% when the humidity sensor-IR CO₂ analyzer was used as the online monitor.²⁴ Generally, the measurement errors of H₂O resulted from three sources: (a) the measurement error from meters, (b) the fluctuation of the H₂O content in the flow gas, and (c) the adsorbed capacity by the transfer pipe in the setup. Therefore, the objective of the present work is to develop a technique with the integration of a dew-point meter and an IR CO₂ analyzer as online monitors for simultaneous measurement of H₂O and CO₂. The surface-flushing humidifier was used to

Q. Y. and S. Y. contributed equally to this study.

[†] To whom correspondence should be addressed.

E-mail: keyangb@zju.edu.cn

Table 1 Physical parameters of the obtained adsorbent used in experiment

Surface area/m ² g ⁻¹	Volume of pores/cm ³ g ⁻¹	Average pore diameter/nm	Particle diameter/mm
20.1	0.386	75.40	0.35 - 0.60

Fig. 1 Diagram of the co-adsorption/desorption experimental setup with simultaneous online measurements of H₂O and CO₂. (1) N₂, (2) CO₂, (3) compressed air, (4) mass flow controller, (5) humidifier, (6) thermostat, (7) tube reactor, (8) dew point meter, (9) gas dryer, (10) infrared gas analyzer, (11) check valve, (12) gas-mixer, (13) three-way valve.

reduce the fluctuation of H₂O content in humid air flow, and the measurement error of H₂O could be further minimized by the water calibration. The proposed technique on the simultaneous online measurement of H₂O and CO₂ would be promising for investigating the co-adsorption/desorption behavior of H₂O and CO₂, especially of direct CO₂ capture from ambient air.

Experimental

Materials

Branched polyethylenimine (PEI, $M_w = 600$) was purchased from Labo Co., Ltd. (Hangzhou, China). Polymethymethacrylate microspheres (mean diameter, ~ 0.45 mm) were obtained from Knowledge & Benefit Sphere Tech. Co., Ltd. (Suzhou, China). Ethanol purchased from JRDUN Biotechnology Co., Ltd. (Shanghai, China) was of AR grade. The adsorbent used in the work was prepared by physically immobilizing PEI into polymethymethacrylate microspheres, where ethanol was used as the solvent. PEI loadings of 20 wt% were obtained when the solvent was evaporated. The physical properties of the obtained adsorbent are provided in Table 1.

Setup for simultaneous online measurements of H₂O and CO₂

A diagram of the co-adsorption/desorption experimental setup with simultaneous online measurements of H₂O and CO₂ is shown in Fig. 1. The setup consisted of a mass-flow controller (D08-2F, Sevenstar Electronics Co., Ltd., China), a humidifier (self-made), a thermostat (AT-950, Automatic Science

Instrument Co., Ltd., China), a $\phi 16 \times 50$ mm stainless-steel tube reactor (self-made), an IR gas analyzer (GXH-510, Xibi Instrument Co., Ltd., China) and a dew-point meter (DP-600, Changdin environmental Tech Co., Ltd., China).

The key parts of the setup were the humidifier and the detectors for the measurements of H₂O and CO₂. The humidifier was made of a sealed cylindrical glass container ($\phi 50 \times 80$ mm) with inlet and outlet stainless-steel tubes ($\phi 3$ mm). The container was placed in a temperature-controlled water bath, and ~ 50 mL of a saturated brine solution was poured into it. The distances between the solution surface and the tube bottoms of inlet and outlet were ~ 12 and ~ 25 mm, respectively. Once dry air had been injected into the glass container from the inlet tube, humid air flow was generated. The desired humidity was obtained by adjusting the temperature of the water bath. It is called the "surface-flushing" method. By means of a mass-flow controller, 0.4 or 1.0 vol% CO₂ gas flow with the desired humidity was obtained by mixing CO₂ gas at the proper ratio with the humid air flow from the humidifier. The detectors for the measurement of H₂O and CO₂ consisted of a dewpoint meter (DP) and an IR gas analyzer, respectively. A dryer filled with silica gel was installed before the IR gas analyzer in order to remove any moisture in the air flow.

Measurement procedure of H₂O and CO₂

Some adsorbents were packed in the tube reactor placed in the thermostat for the co-adsorption/desorption experiment. Prior to this measurement, the adsorbents were heated to 50°C under the N₂ flow rate at 100 mL/min for two hours in order to remove the adsorbed CO₂ and H₂O. The CO₂ and H₂O adsorption/desorption amounts could be determined by using the weight method. For the co-adsorption test, humidified gas flow containing 0.4 vol% CO₂ was passed through the adsorbent at a rate of 100 mL/min at 20°C. The H₂O and CO₂ concentrations of the outlet gas flow from the tube reactor were simultaneously monitored with a DP and an IR gas analyzer, respectively. The passing N₂ at a rate of 100 mL/min under the elevated temperature (usually at 30°C) through the adsorbent was used for the desorption process. The co-desorption of H₂O and CO₂ would take place, and the corresponding concentrations of the outlet gas flow were also monitored.

The uptake of H₂O or CO₂ on the adsorbent over the adsorption time, q_a (mg H₂O or CO₂/g adsorbent), was calculated by integrating the corresponding breakthrough curves:

$$q_a = \int_{t=0}^{t=t_a} \frac{Q_a(c_0 - c_1)M}{m_s \times V_m} dt, \quad (1)$$

where t_a (min) is the adsorption time, V_m is 22.4 L/mol, M (g/mol) is the molecular mass of CO₂ (or H₂O), Q_a (mL/min) is the volumetric flow rate of the gas flow, m_s (g) is 1.0011 g for the mass of the adsorbent in the tube reactor, and c_0 and c_1 (vol%) are the CO₂ (or H₂O) concentrations from the inlet and outlet gas flows, respectively.

Similarly, the amount of CO₂ (or H₂O) desorbed over desorption time, q_d (mg CO₂ or H₂O/g adsorbent), was calculated by the integrating the corresponding desorption curves,

$$q_d = \int_{t=0}^{t=t_d} \frac{Q_d c M}{m_s \times V_m} dt, \quad (2)$$

where t_d (min) is the desorption time, V_m is 22.4 L/mol, M (g/mol) is the molecular mass of CO₂ (or H₂O), c (vol%) is the CO₂ or H₂O concentration in the outlet gas flow (the H₂O concentration was transferred from DP), and Q_d (mL/min) is the

volumetric flow rate of N₂.

Results and Discussion

Generation of humid air flow

Humidification was usually obtained by bubbling air flow through water at a particular temperature.²⁰ To reduce the fluctuation of H₂O content and to gain a low H₂O content of air flow, surface-flushing was used to humidify the air flow. Figure 2 shows the relationships between the humidity of the air flow and the temperature of the water bath for both the bubbling and surface-flushing methods. The polynomial fitting results are also given.

It was observed that the water concentration in the air flow increased with an increase of the water bath temperature in both cases. For the bubbling, the H₂O contents of 0.773–3.256 vol% were generated within the temperature range of –7–30°C. Whereas for the surface-flushing, 0.385–3.155 vol% were generated within –7–35°C. This reveals that the surface-flushing method generated air flow with a lower H₂O content than did the bubbling method within the experimental conditions.

On the basis of taking the derivative of polynomials (a) and (b) in Fig. 2, the corresponding derivations could be obtained as follows:

Fig. 2 Relationships between the humidity of air flow and temperature of (a) the bubbling approach, (b) the surface-flushing approach. Polynomial a (bubbling): $c = 0.00181T_2 + 0.02525T + 0.86566$, $R^2 = 0.99965$. Polynomial b (surface-flushing): $c = 0.00143T_2 + 0.02535T + 0.48496$, $R^2 = 0.99927$.

$$\text{bubbling: } c' = 0.00362T + 0.02525, \quad (3)$$

$$\text{surface-flushing: } c' = 0.00286T + 0.02535. \quad (4)$$

The obtained value of c' for the surface-flushing method was lower than that for bubbling at the given temperature, since the slope of Eq. (4) is smaller than that of Eq. (3). Accordingly, it indicates that the humidity of the air flow increased more smoothly with increasing bath temperature in the surface-flushing method. For instance, a humidity of 0.41% would be changed for the surface-flushing method when experiencing a 5°C increase or decrease at 20°C, whereas 0.49% would be changed for the bubbling method. This reveals that the control of the H₂O content in air flow for the surface-flushing method will be more stable and accurate and its fluctuation would be reduced.

Deviation of measurement

The single-component H₂O or CO₂ adsorption/desorption experiments were conducted in order to check the reliability of the measurement. The adsorption or desorption amounts could be calculated by Eqs. (1) and (2) based on the integration of the breakthrough or the elution curves, and the weight method of the adsorbents could also be determined. The obtained results and corresponding relative errors (RA) are presented in Table 2. It is observed that the adsorption amount of H₂O calculated by the integration is larger than that determined by the weight, especially for the case of the low H₂O content in the air gas. The values of RA are close to 1% either for the CO₂ adsorption or for the CO₂ desorption, indicating that the online measurement of CO₂ is reliable. The H₂O measurement in the desorption process can also be reliable, since the RA is close to 1%. Furthermore, the variations of the H₂O uptake at an H₂O content of 1% on the adsorbent against the adsorption time determined by the weight and calculated by the integration are presented in Fig. 3. It was observed that the differences of the obtained H₂O uptake between the integration and the weight increased with increasing the adsorption time. The H₂O uptake calculated by the integration is as high as 18% by weight at an operating time of 85 min. This means that the H₂O uptake integrated by Eq. (1) based on the breakthrough curve is higher than the actual value. It could be explained that some of H₂O was adsorbed on the transfer pipe before the DP monitor during the adsorption process, since the partial pressure of H₂O in the outlet gas flow gradually increased after H₂O broke through the adsorbent. Therefore, the breakthrough curve of H₂O generated would be lower than the real one. Due to the error-amplification in Eq. (1), the error of the H₂O measurement might be significant, even if only a little amount of H₂O was adsorbed by the transfer pipe. Herein, the online measurement of H₂O in the adsorption process should be corrected further, and water calibration would

Table 2 Single-component H₂O or CO₂ adsorption/desorption amounts

	q for 1.69% (vol) H ₂ O (mg/g adsorbent)			q for 1.37% H ₂ O (mg/g adsorbent)			q for 1% H ₂ O (mg/g adsorbent)			q for 0.4% dry CO ₂ (mg/g adsorbent)		
	A_w	A_i	RA, %	A_w	A_i	RA, %	A_w	A_i	RA, %	A_w	A_i	RA, %
Adsorption ^a	108.4	110.4	+1.85	61.5	63.1	+2.60	54.5	64.3	+17.98	38.9	39.4	+1.29
Desorption ^b	108.3	107.7	–0.55	61.6	62.1	+0.81	54.7	54.1	–1.10	38.5	38.9	+1.04

a. 20°C, gas flow rate: 100 mL/min, b. 50°C, N₂ flow rate: 100 mL/min. A_w , the amount of adsorption/desorption was determined by the weight method, mg/g. A_i , the amount of adsorption/desorption was calculated by the integration of the breakthrough or elution curves, mg/g.

Fig. 3 Variation of the H₂O uptake on the adsorbent against the adsorption time (H₂O in inlet flow: ~1 vol%; adsorption temperature: 20°C; flow rate: 100 mL/min).

Fig. 4 H₂O breakthroughs curves at different H₂O contents with and without water-calibration modes.

be conducted. In addition, it has been noticed that the effect of the H₂O desorption can be ignored, since the transfer pipe was flushed by dry N₂ in the desorption process.

Water calibration

The adsorption amount of H₂O on the transfer pipe should be subtracted for the calculation of the adsorption amount on the adsorbents. Water calibration was conducted where no adsorbent was packed in the tube reactor, and the operating condition was the same as that of H₂O adsorption. Figure 4 presents the H₂O breakthrough curves at H₂O contents of 1.00, 1.37 and 1.69% with and without adsorbents. The H₂O uptake on the adsorbent with the water calibration would be revised according to the following equation:

$$q_a' = \int_{t=0}^{t=t_s} \frac{Q_a(c_0 - c_1)M}{m_s \times V_m} dt - \int_{t=0}^{t=t_s} \frac{Q_a(c_0 - c_1')M}{m_s \times V_m} dt, \quad (5)$$

where c_1' is the H₂O concentration in the outlet gas flow in the water-calibration mode.

Table 3 Results obtained with water calibration in the adsorption of H₂O

Calibration	q for 1.69% H ₂ O (mg/g sorbent)		q for 1.37% H ₂ O (mg/g sorbent)		q for 1.00% H ₂ O (mg/g sorbent)	
	Cal.	RA, %	Cal.	RA, %	Cal.	RA, %
With	107.1	-1.20	60.8	-1.14	56.7	+4.04
Without	110.4	+1.85	63.1	+2.60	64.3	+17.98

Fig. 5 Breakthroughs of CO₂ and H₂O in the adsorption processes (concentration of CO₂ in inlet flow, 1%(v); concentration of H₂O in inlet flow, ~1%(v); adsorption temperature, 20°C; gas-flow rate, 100 mL/min).

Fig. 6 Elution curves of CO₂ and H₂O in the desorption processes (desorption temperature, 50°C; N₂ flow rate, 100 mL/min).

The obtained results with the water calibration on the basis of Eq. (5) in the adsorption of H₂O are presented in Table 3. The relative errors were calculated compared with the weight method. It was observed that the RA were significantly reduced, especially in the case of a low H₂O content. Although the RA of 4.04% at 1% H₂O is higher than that at 1.37 or 1.69%, the accuracy of the H₂O measurement can be acceptable since a

Table 4 Measurement results of CO₂ and H₂O with water calibration in the adsorption/desorption of humid CO₂ process

	A ₁ H ₂ O	A ₁ CO ₂	A ₁ H ₂ O + CO ₂	A _w	RA, %
Adsorption	69.4	41.2	110.6	106.6	+3.75
Desorption	66.7	41.6	108.3	109.1	−0.73

The meanings of the symbols of A₁ and A_w, both in mg/g adsorbent, are the same as those in Table 2.

lower H₂O content would result in a higher error induced by the integration.

Simultaneous online measurements of CO₂ and H₂O

The resulting breakthrough of adsorption and the elution curves of desorption on the co-adsorption/desorption of H₂O and CO₂ are presented in Figs. 5 and 6, respectively, where the performances of dry CO₂ (0.4 vol%) were also investigated in comparison. It can be observed that the online measurements of H₂O and CO₂ concentrations were successfully achieved in the co-adsorption/desorption system.

The results obtained by simultaneous online measurements of CO₂ and H₂O with water calibration in the co-adsorption/desorption of humid CO₂ process are presented in Table 4. Here the results determined by the weight are listed for comparison. It is as expected that the measured RA in the adsorption process at a low H₂O content of H₂O/CO₂ = 1:0.4 is as high as 3.75% due to the H₂O adsorption on the transfer pipe and amplification of the measurement error. Moreover, it has been shown that the measured RA values of CO₂ and H₂O with water calibration in the desorption process at an H₂O content of H₂O/CO₂ = 1:0.4 is lower than 0.1%. Therefore, it demonstrated that the technique for the simultaneous online measurements of CO₂ and H₂O in the humid CO₂ co-adsorption/desorption process was successfully conducted, and that the measurement accuracy was both reliable and acceptable for investigating the corresponding behavior.

Conclusions

The setup assembled with a DP and an IR CO₂ analyzer in series was developed for simultaneous online measurements of CO₂ and H₂O in the humid CO₂ co-adsorption/desorption process. Surface-flushing on a saturated brine solution was used to humidify the air flow, which can improve the controllability of the humidity in this air flow and reduce any fluctuation of the H₂O content as well. The measurement error of H₂O can be significantly reduced by the water calibration. It has been demonstrated that the RA for simultaneous measurements of CO₂ and H₂O are lower than 0.1% in the desorption process. The high RA in the adsorption of H₂O is attributed to H₂O adsorption on the transfer pipe and amplification of the measurement error. The measurement accuracy in the setup is qualified for the investigation of co-adsorption/desorption behavior of H₂O and CO₂, especially for direct CO₂ capture from ambient air in a confined space.

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