Springer

KSME

Journal of Mechanical Science and Technology 26 (8) (2012) 2285~2290
www.springerlink.com/content/1738-494x
DOI 10.1007/s12206-012-0609-y

CO_2 absorption characteristics of nanoparticle suspensions in methanol †

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(Manuscript Received November 14, 2011; Revised April 6, 2012; Accepted May 23, 2012)

Abstract

Recently there have been growing concerns that anthropogenic carbon dioxide (CO_2) emissions cause the global warming problem. Therefore, the cutting-edge technologies for the reduction, separation and collection of the CO_2 are very important to alleviate this problem. The best methods for reducing the CO_2 emission are to increase the energy efficiency and to remove it from the power plant. The CO_2 absorption from the syngas in the integrated gasification combined cycle (IGCC) might increase the energy efficiency of the power generation systems, which also contribute to mitigate the global warming. In this study, the suspensions of nanoparticles in methanol (called the nanofluid) are developed and estimated to apply it to absorb CO_2 gas in the IGCC systems. The nanofluids are prepared by the ultrasonic treatment and show the good stability. It is found that the CO_2 absorption rate by the nanofluid is enhanced up to ~8.3% compared to the pure methanol.

Keywords: CO_2 absorption; Methanol solution; Nanofluid; Particle motion

1. Introduction

The shortage of oil resources will increase the price of the crude oil, petrochemicals and natural gas in near future. So the synthetic natural gas (SNG) from the coal is one of the promising alternative energy resources. An integrated gasification combined cycle (IGCC) is a power plant system using the synthesis gas (syngas). In the IGCC, there needs to remove the acid gases such as carbon dioxide (CO_2) and hydrogen sulfide (H_2S) from valuable feed gas streams. By doing so, the feed gas can be made more suitable for combustion and further processing. The ways to remove the CO_2 are absorption, adsorption, membranes, cryogenics, chemical looping and etc. [1-6]. Recently, Rectisol system, that is physical absorption type, is used prevalently to remove the acid gases. This system uses methanol as an absorbent. The advantages of methanol absorbent are cheap and selective absorption of acid gases such as CO_2, H_2S and COS. In the Rectisol system, the temperature of methanol absorbent is maintained about -40^{o}C to increase the absorption rate according to the Henry's solubility law. Therefore, much energy is required to keep such a low temperature of methanol. One of the promising methods to enhance the CO_2 absorption is to use the suspensions of nanoparticles (called nanofluid) in the absorbent. It had been reported that the nanofluids increased mass transport compared to the base fluids [3, 7-11]. Therefore nanofluids have been paid extensively attention for heat and mass transfer enhancement as the next-generation working fluids. For an example of CO_2 absorption, the silica/water nanofluid was synthesized to apply to the CO_2 absorption process [3]. The authors reported that the addition of nanoparticles increased the average absorption rate of 76% during the first 1 minute and total absorption amount of 24% at 0.021 wt% of silica nanoparticle. Such a high increase of CO_2 absorption rate was realized based on the water base fluid because the CO_2 absorption rate in water was not so good.

In this study, we tried to enhance the CO_2 absorption rate to save the energy required to maintain the low temperature of the methanol absorbent. The particles (i.e. alumina in this study) and methanol (base fluid) are combined into alumina/methanol nanofluids to enhance the CO_2 absorption rate of the base fluid. The parametric analysis on the effects of particle fraction and absorbent amount on CO_2 absorption rate are carried out. The nanofluids are prepared by the ultrasonic treatment and show the good dispersion stability. The suspensions of nanoparticles in absorbents are expected to be a promising candidate for removing acid gases as well as CO_2.

2. Experimental section

2.1 Experimental apparatus and procedure

Fig. 1 is the schematic diagram of the experimental appara-

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† Recommended by Associate Editor Dongsik Kim

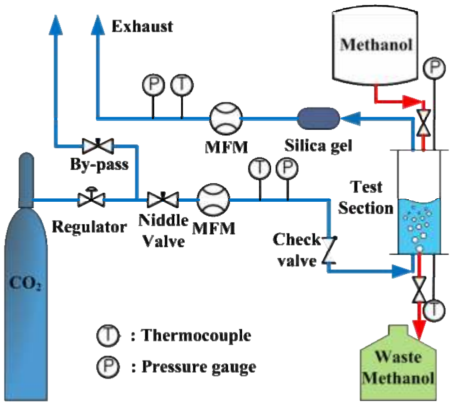


Fig. 1. Schematic of experimental apparatus.

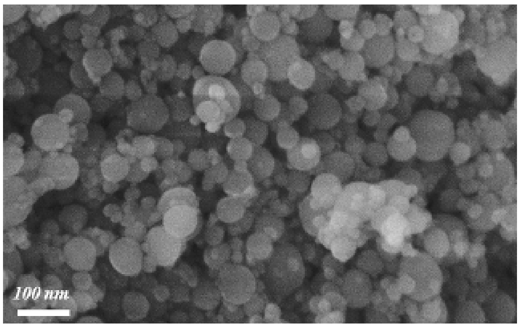


Fig. 2. FE-SEM images of alumina nanoparticles tested in this study.

tus. The amount of feed gas is controlled by the regulator at the outlet of CO_2 tank and the gas flow rates are measured by two mass flow meters at the inlet and outlet of test section. Silica gel is used to remove the existing water vapor in the outlet of the test section. The silica gel adsorbs water vapor selectively, and has no effect on CO_2 gas under the present experimental cases although silica gel can adsorbs the CO_2 gas under the closed and water vapor free conditions [12]. Therefore, the CO_2 amount is accurately measured by the mass flow meter at the outlet of the test section. An air-stone nozzle is used to produce a minimum bubble size at the bottom of the test section. The temperature of test solution is automatically monitored and controlled by a set of thermocouple and thermostat.

The absorbents are prepared by the following two-step method. First, the alumina nanoparticles are prepared (supplied by the Nanophase Tech., USA). Fig. 2 shows a FE-SEM image of the alumina nanoparticles tested in this study. Second, the particles are dispersed into the base fluid by the ultrasonication process to form the stable absorbents. The particle concentrations of absorbents range from 0.005 to 0.1 vol%. To evaluate the dispersion stability of nanofluids, the hydrodynamic diameters of the particles are measured by the dynamic scattering method (ELS-Z, Otsuka Elec., JPN) and the dispersion stability of nanofluids is visualized in vials for 24 hrs. Fig. 3 shows the size distribution of the nanoparticles (volume base) suspended in nanofluid. The average size of the nanoparticle cluster is measured about 200 nm. The original powder size of the alumina nanoparticle is 40~50 nm. The CO_2 absorption experiments are carried out at the 10 °C. Table 1 shows the geometric conditions of the test section and experimental conditions.

Table 1. Geometric conditions of the test section and experimental conditions.

CO_2	
Purity	99.999%
Inlet mass flux	3.05×10^{-5} kgs^{-1}
Inlet pressure	103 kPa
Methanol	
Purity	99.8 %
Temperature	10°C
Amount	200 ~ 500 mL
Al_2O_3	
Particle powder size	40~50 nm
Concentration	0.005 ~ 0.1 vol%
Test section	
Diameter	70 mm
Height	260 mm
Ultrasonication	
Time	1 hr
Power	750 W
Frequency	20 kHz

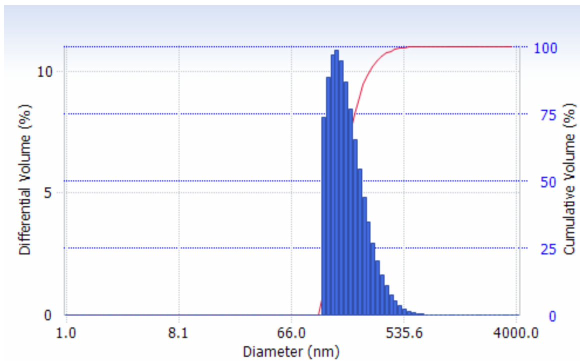


Fig. 3. The size distribution of the nanoparticles (volume base) suspended in nanofluids.

2.2 Data reduction

The experimental data of the pressure, temperature and gas flow rate are obtained every 10 seconds for 140 seconds by the Vee program (Agilent Tech.). The CO_2 absorption rates are obtained using Eq. (1),

$$\dot{m}_{abs} = \frac{\int \dot{m}_{inlet} dt - \int \dot{m}_{outlet} dt}{\Delta t} \tag{1}$$

where $\dot{m}_{inlet}$ and $\dot{m}_{outlet}$ are the gas flow rates at the inlet and the outlet of the test section, respectively. The effective absorption ratio R_{eff} is defined as the ratio of the absorption rate of the mixture to that of the pure methanol, which is expressed as,

$$R_{eff} = \frac{\dot{m}_{abs,nf}}{\dot{m}_{abs,bf}} \quad (2)$$

where $\dot{m}_{abs,nf}$ and $\dot{m}_{abs,bf}$ are the absorption rates for the nanofluid and that for the base fluid, respectively. Experimental error could be estimated using Eq. (3) suggested by Holman [13], being estimated within 7%.

$$Error_{ex} = \sqrt{\left(\frac{U_{\dot{m}_{\max,i}}}{\dot{m}_{\max,i}}\right)^2 + \left(\frac{U_{\dot{m}_{\max,o}}}{\dot{m}_{\max,o}}\right)^2 + \left(\frac{U_{P_{\max}}}{P_{\max}}\right)^2 + \left(\frac{U_{T_{\max}}}{T_{\max}}\right)^2 + \left(\frac{U_{M_{\max}}}{M_{\max}}\right)^2} \quad (3)$$

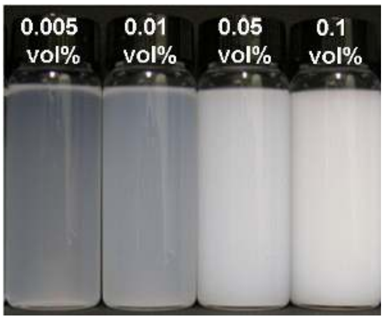
$U_{\dot{m}_{\max,i}}$: Mass flow rate error from the maximum mass flow rate in the inlet
$\dot{m}_{\max,i}$: Maximum mass flow rate in the inlet
$U_{\dot{m}_{\max,o}}$: Mass flow rate error from the maximum mass flow rate in the outlet
$\dot{m}_{\max,o}$: Maximum mass flow rate in the outlet
$U_{P_{\max}}$: Pressure error from the maximum pressure
$P_{\max}$: Maximum pressure
$U_{T_{\max}}$: Temperature error from the maximum temperature
$T_{\max}$: Maximum temperature
$U_{M_{\max}}$: Scale error from the maximum mass scale
$M_{\max}$: Maximum mass scale

An electronic balance was used to weigh the amount of methanol. The mass of the methanol used in this study was 158 g (which is the maximum mass scale) at which the scale error of the equipment is 0.5 g.

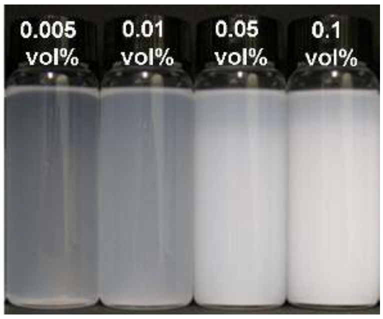
3. Results and discussion

3.1 Dispersion stability

In nanofluids, stable suspension of the nanoparticles is required to obtain its proper working. The hydrodynamic diameter of the nanoparticles suspended in nanofluids should be below the critical size to be suspended stably in the base fluid. If the nanoparticle size exceeds its critical size, the nanoparticle will be sedimented due to the gravitational force. The critical size for the dispersion stability can be determined by considering the repulsion force due to the Coulomb force and the attraction one due to the van der Waals force [14]. Fig. 4 shows the photos of the prepared alumina/methanol absorbents with the particle concentrations and time. The particles in the absorbents are kept stably for 24 hrs.



(a) Just after preparing nanofluids



(b) After 24 hrs

Fig. 4. Photos of the prepared alumina/methanol absorbents: (a) just after preparing nanofluids; (b) after 24 hrs.

To evaluate more precisely the dispersion stability of nanoparticles, the hydrodynamic diameters of the nanoparticles were measured and the measured ones were compared with the theoretical values estimated. Jung et al. [14] proposed a dimensionless group, G' to determine a critical size to obtain the good dispersion stability of nanoparticles as follows:

$$G' = \frac{1}{3}\pi\left(\rho_p - \rho_{bf}\right) g \sqrt{\frac{2r^5\tau_p}{3\mu k_B T}} \quad (4)$$

where ρ_p and ρ_{bf} are the densities of particle and base fluid, μ is the viscosity of the base fluid, r is the radius of the particle, τ_p ($= l_{np}/\overline{u}_{Br}$, l_{np} is the mean free path of the nanoparticle and $\overline{u}_{Br}$ is its Brownian velocity) the relaxation time of particle which is the period between consecutive collisions or encounters with another particle, k_B is the Boltz mann constant and T is the temperature, respectively, and is the acceleration due to gravity. As the value of G' decreases, the nanofluid becomes more stable and the critical diameter of the particles for good dispersion stability can be obtained from Eq. (4) with the G' value of 1.0. The critical sizes estimated by the theoretical approach for the alumina/methanol nanofluids range from 1.1 to 1.8 μm for the present experimental cases as shown in Fig. 5. Fig. 6 shows the measured hydrodynamic diameters of the particles in alumina/methanol absorbents with day. It was found that the measured diameters were kept below ~210 nm. Since the measured hydrodynamic di-

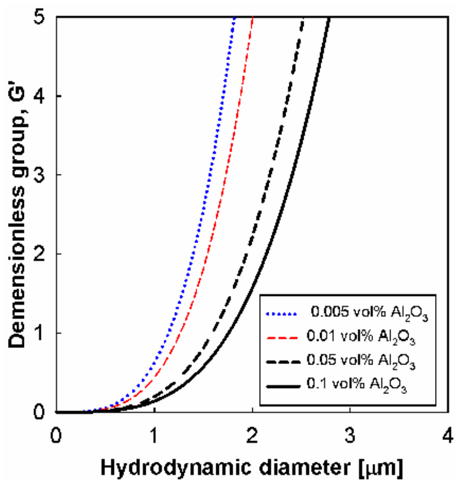


Fig. 5. Critical size of the particles for good dispersion stability in alumina/methanol nanofluids.

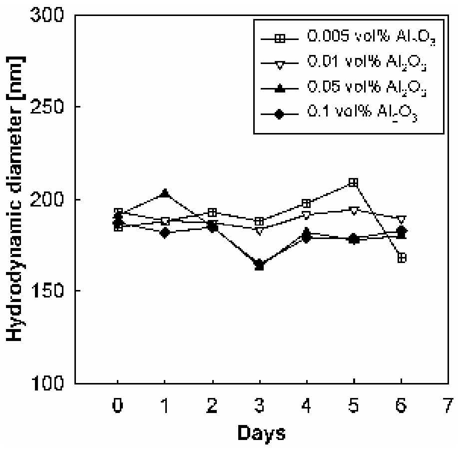


Fig. 6. Variations of the hydrodynamic diameters of the particles in alumina/methanol nanofluids with day.

ameters are smaller than the critical sizes, it can be said that the prepared absorbent are stable, which is in good agreement with the experimental results (as shown in Figs. 4 and 6).

3.2 Effect of absorbent amount on CO_2 absorption

The main effects of the nanoparticles in absorbents on the CO_2 absorption are the particle-laden flow of methanol due to the Brownian motion, and the mixing flow of the methanol and the CO_2 to enhance the absorption rate under given conditions. To find an optimal amount of the absorbent, we tested 4-cases with different amounts (200, 300, 400 and 500 ml) of the absorbent. All experimental conditions except the absorbent amount were fixed. Fig. 7 shows the effective absorption ratio depending on the absorbent amount for the 0.01 vol% of alumina particles. The effective absorption ratio decreases with increasing absorbent amount because the effects of the Brownian motion and the mixing flow due to the nanoparticles decrease. As the absorbent amount increases under the

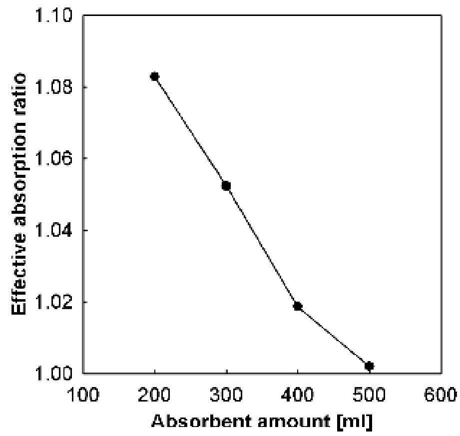


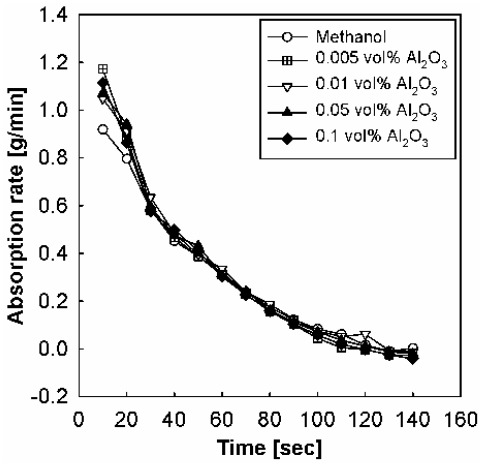
Fig. 7. Effective absorption ratio depending on the absorbent amount for the 0.01 vol% of alumina particles.

same experimental conditions, the height of absorbent in the test section becomes higher. There is a wider diffusion regime compared to the lower height one due to the forced and/or natural convections of the solution under the confined chamber diameter. As a result, the effect of the nanoparticles on the CO_2 absorption decreases under the well-mixing condition by the convections while the effect of the particle-laden flow on the CO_2 absorption relatively increases under the lower height case. Hereafter we fixed the 200 ml (lower height case) of the absorbent amount to examine the particle concentration effect on the absorption rate and amount of CO_2.

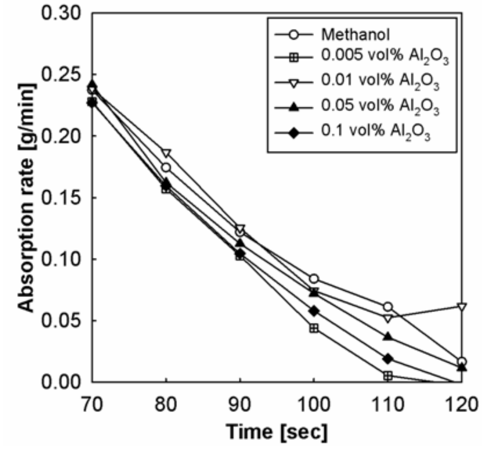
3.3 Effect of particle concentration on the absorption rate and amount

Figs. 8 and 9 show the CO_2 absorption rates and amount for different particle concentration with time, respectively. The absorption rates of the absorbents containing alumina particles are higher than that of the pure methanol absorbent at the early stage of absorption as shown in Fig. 8(a). At the final stage, the absorption rate of 0.01 vol% of the particles becomes higher than those of other nanofluids cases as shown in Fig. 8(b). By integrating the absorption rate for 140 seconds, it is found in Fig. 9 that the total absorption amount of 0.01 vol% is the highest, which means that the average absorption rate of 0.01 vol% is higher than those of the other concentrations

Fig. 10 shows the effective absorption ratio for each particle concentration. It is found that the maximum CO_2 absorption enhancement compared to the pure methanol is 8.3% at 0.01 vol% of alumina particle. To the 0.01 vol% alumina particles in the absorbents, the effective absorption ratio increases with increasing the particle concentration. However, after that point, the effective absorption ratio decreases with increasing the particles concentration, which means there is an optimal particle concentration to obtain the maximum absorption rate. The reason is that the mixing effect of nanoparticles is due to the particle-laden flow induced by its Brownian motion, however if the particle concentration increases over a critical value,



(a)



(b)

Fig. 8. Absorption rates for the different particle concentrations with time (a) and an enlarged view of the selected region (b).

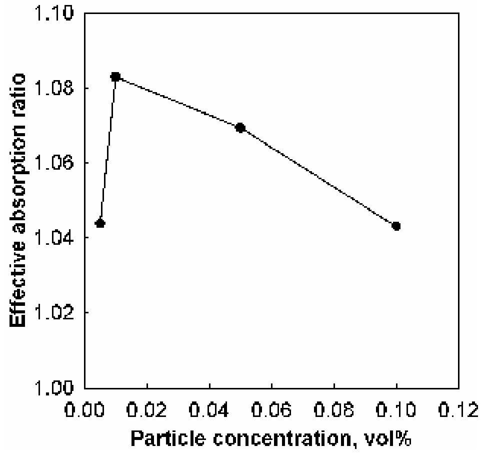


Fig. 9. Absorption amounts for the different particle concentrations with time.

there is less Brownian motion because the inter-particle interaction hinders its motion.

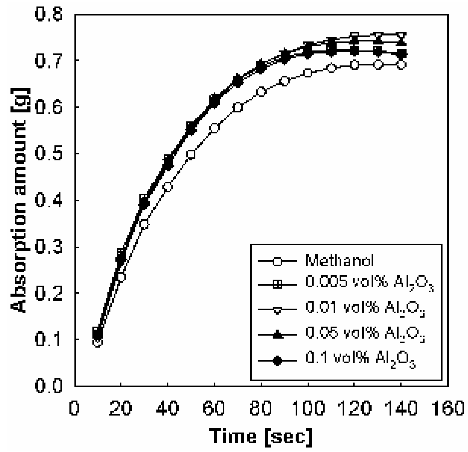


Fig. 10. Effective absorption ratio depending on the particle concentration.

3.4 Absorption enhancement mechanism for nanofluids

There are several mechanisms to explain the gas absorption enhancement of colloid systems. For example, the hydrodynamic effect model proposes that the particles may increase the specific interfacial area by covering the bubble surface and preventing the coalescence of the bubbles, resulting in smaller bubbles [9]. Another one is that the particles may produce local turbulence and refresh the gas-liquid boundary layer by mixing it into the bulk liquid [15]. However, the general mechanism of the mass transfer enhancement is still debating. The most accepted mechanism has been proposed by Krishnamurthy et al. [16]. They argued that the Brownian motion of the nanoparticles was not directly responsible for the mass transfer enhancement, but mainly due to the velocity disturbance field in the fluid created by the motion of the nanoparticles. Also, the particles collide with the gas-liquid interface, consequently breaking the bubble into smaller bubbles [3]. The smaller bubbles having same volume with primary one mean larger interfacial area which increases mass transfer from gas to the base liquid. In this study, it was confirmed that the enhanced CO_2 absorption was induced by both of mixing and breaking gas-bubbles due to the motion of nanoparticles.

4. Conclusions

Recently there are growing concerns that anthropogenic carbon dioxide (CO_2) emissions cause the global warming problem. To mitigate the problem, the important of energy efficiency and the reduction of CO_2 are so important. Here, we tried to enhance the CO_2 absorption rate to save the energy to maintain the low temperature of the methanol absorbent. The parametric analysis on the effects of particle fraction and absorbent amount on CO_2 absorption rate and amount were carried out. The nanofluids were prepared by the ultrasonic treatment and show the good stability. It was found that the CO_2 absorption rate by the nanofluids was enhanced up to ~8.3% compared to the pure methanol. The suspensions of nanoparticles in absorbents are expected to be a promising candidate for removing acid gases as well as CO_2.

Acknowledgment

This work was supported by a grant from Kyung Hee University in 2010 (KHU-20100186).

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