Preparation of nanofluids and their applications in enhanced CO₂ absorption

Huiyu Han¹, Xiaoxun Ma¹ and Long Xu¹*
¹School of Chemical Engineering, Northwest University, International Science & Technology Cooperation Base of MOST for Clean Utilization of Hydrocarbon Resources, Chemical Engineering Research Center of the Ministry of Education for Advanced Use Technology of Shanbei Energy, Shaanxi Research Center of Engineering Technology for Clean Coal Conversion, Collaborative Innovation Center for Development of Energy and Chemical Industry in Northern Shaanxi, Xi’an, 710069, PR China.
*Corresponding author’s e-mail: longxuxulong@163.com

Abstract: Nanofluids opened up research in the field of thermal energy and mass transfer engineering when it was first proposed by American scientist Choi. In this paper, a two-step method was used to prepare stable nanofluids. Enhancement factor was introduced to study the enhancement of CO₂ absorption by nanofluids under different experimental conditions. The results show that the enhancement of the three nanoparticles in the same solid content is TiO₂ > Al₂O₃ > SiO₂; The optimum solid content of SiO₂ and Al₂O₃ is 0.8 g/L, and the optimum solid content of TiO₂ is 0.6 g/L; Within the scope of this study, the larger the particle size, the better the absorption effect. As the organic amine concentration increases, absorption of solution improves.

1. Introduction
In 1969, Ramachandran and Sharma first theoretically inferred that for slurry systems with fast chemical reactions and sparingly soluble particles, the particles would significantly accelerate the rate of gas absorption[1]. Later, Kars et al. used the stirred tank to study the effect of activated carbon particles on the gas-liquid mass transfer in the Na₂SO₃-O₂ absorption system, and confirmed the existence of the strengthening effect[2]. This discovery motivates that we will expand our research into nanoscale particles[3-5].

In 1995, the concept of nanofluids was first proposed by Choi from the National Laboratory of Argonne, USA that Nanofluids are stable and uniform two-phase suspensions are obtained by dispersing nanoparticles in an organic or inorganic liquid medium in a certain proportion and manner[6]. In theory, nanofluids belong to a colloidal dispersion system, and its properties are related to the properties, content, scale, shape and physical and chemical properties of the nanoparticles[7-10].

The concept of nanofluids was first applied to the field of heat transfer. These studies have basically found that the addition of nanoparticles can increase the thermal conductivity of the base fluid, providing a new idea for enhancing heat transfer[11]. According to the similarity between heat transfer and mass transfer, nanoparticles should also affect the mass transfer process inside the fluid. Therefore, research on mass transfer in nanofluids has also begun.
At present, the research on gas-liquid mass transfer of nano-particles is mainly focused on the physical absorption of insoluble gases. There are few studies on the absorption process of chemical reactions. Therefore, the effect of nanoparticles on gas-liquid mass transfer in the presence of chemical reactions was studied in the context of organic amines absorbing CO$_2$[12]. In this paper, 20nm, 40nm and 60nm SiO$_2$, TiO$_2$ and Al$_2$O$_3$ nanoparticles were used, and MEA and MDEA with large difference in absorption rate were selected to prepare nanofluids with good stability. The effects of particle parameters such as nanoparticle type, particle size and solid content on absorption were studied.

2. Experimental section

2.1. Preparation of nanofluids

In this experiment, nanofluids was prepared by a two-step method. Firstly, Monoethanolamine (AR, Tianjin Komio Chemical Reagent Co., Ltd.), N-Methyldiethanolamine (99%, Tianjin Komio Chemical Reagent Co., Ltd.) having a mass fraction of 30% was separately disposed, and the nano-SiO$_2$, TiO$_2$, Al$_2$O$_3$ (Hebei Gegui Welding Material Co., Ltd.) was weighed according to the solid content of 0.4-1.6 g/L with an electronic balance (Shenyang Longteng Electronics Co., Ltd.), and added to the solution. The mixture was stirred for 20 min with a DF-101S collector-type constant temperature heating magnetic stirrer (Zhengzhou Kefeng Instrument Equipment Co., Ltd.), and ultrasonically dispersed for 40 min using a ultrasonic cell pulverizer (Ningbo Xinyi ultrasonic equipment Co., Ltd.).

2.2. Stability of nanofluids

The advantage of the "two-step method" is that it is easy to operate and is suitable for the preparation of most nanofluids. The disadvantage is that the prepared nanofluids have poor stability. In order to reduce this effect, Generally, we will add appropriate dispersing agents or surface chemical modification of the nanoparticles during the preparation process[13].

In this experiment, four different types of dispersing agents, sodium dodecyl benzene sulfonate(AR,Tianjin Tianli Chemical Reagent Co., Ltd.), sodium polyacrylate(AR, Tianjin Damao Chemical Reagent Factory), Triton X-100(AR, Xibao Biotechnology Co., Ltd.), N, N, N-trimethyl-1-dodecanaminium bromide(99%, Tianjin Dengfeng Chemical Reagent Factory), were selected. Figure 1 shows the morphology of the nanofluids with four dispersants added in sequence after standing for 24 h. It can be seen from the figure that the nanofluid with sodium dodecyl benzene sulfonate has no obvious precipitates, indicating that the dispersant basically meets the experimental requirements.

![Figure 1. Effect of dispersant on the stability of nanofluids.](image)

1-Nanofluid prepared by adding sodium dodecyl benzene sulfonate; 2-Nanofluid prepared by adding sodium polyacrylate; 3-Nanofluid prepared by adding Triton X-100; 4-Nanofluid prepared by adding N, N, N-trimethyl-1-dodecanaminium bromide.

Chemical modification refers to the use of a chemical reagent as an intermediate medium to bind nanoparticles to a base liquid molecule. 1.5 g of nano-SiO$_2$ was ultrasonically dispersed in 14 mL of toluene, 0.6 g of triethylamine was added and stirred uniformly, by the addition of 0.8 g of trimethyl
chlorosilane, and condensed and refluxed at 120 °C for 4 h. The obtained suspension was centrifuged, and the precipitate was washed five times with toluene, after vacuum drying at 60 °C, the surface-grafted modified nano-SiO2 spheres were fabricated.

2.3. Nanofluid enhanced mass transfer

2.3.1. Introduction to experimental equipment and principles. As shown in figure 2, N2 and CO2 are depressurized by a pressure reducing valve and then enter the mass flow device to control the total mixed gas flow rate of 67 mL/min, and the initial volume fraction of CO2 is 10.45%. The mixed gas enters the absorption liquid from the nozzle at the bottom of the absorber. During the ascending process, a part of CO2 is absorbed, and the other part is discharged with the N2 from the upper outlet of the absorber. After the exhaust gas is dried, it enters the infrared flue gas analyzer, and the CO2 absorption and absorption rate are calculated by measuring the CO2 volume fraction in the exhaust gas for characterization. To characterize the absorption capacity of the absorption liquid for CO2.

2.3.2. Data analysis method. In order to reflect the difference in absorption capacity between the two-component nanofluid and the organic amine solution, we introduce an absorption enhancement factor:

\[
E = \frac{V_{CO_2-nanofluid}}{V_{CO_2-pure-solution}}
\]

(2-1)

3. Experimental results and discussion

3.1 Nanoparticle-MDEA Nanofluid Absorption Experiment

Figure 3 shows the breakthrough curves of 40nm, 0.4-1.6 g/L TiO2-MDEA nanofluid and MDEA solution. The figure shows that the volume fraction of CO2 in the exhaust gas of the nanofluid experiment is lower than that of the blank experiment, indicating that more CO2 is absorbed, which proves that the addition of TiO2 nanoparticles enhances the absorption of CO2.

Figure 3. Comparison of MDEA blank solution and TiO2 nanofluid absorption experiment.
Figure 4 compares the variation of the enhancement factors of TiO₂, SiO₂ and Al₂O₃ with the solid content, the particle size is the same as 40nm. The enhancement effect of the four nanoparticles at the same solid content is TiO₂>Al₂O₃>SiO₂. SiO₂, even appears to hinder absorption. Because the SiO₂ nanoparticles are highly hydrophilic, causing an increase in the viscous resistance of the particle motion and a decrease in the disturbance to the mass transfer boundary layer; TiO₂ particles have a certain adsorption effect on CO₂, so their enhancement factor is larger than other particles.

![Figure 4](image)

Figure 4. Effect of nanoparticle types on absorption enhanced ticks.

For the same type of nanoparticles, increasing the solid content means an increase in the number of particles, and the possibility of agglomeration of the nanoparticles increases. In addition, the surface tension and dynamic viscosity of the nanofluids also change slightly, which respectively affect the detachment radius of the bubble at the nozzle and the residence time in the liquid phase[14]. Figure 5 shows the variation of the enhancement factor of several nanoparticles used in the experiment with the solid content. The optimum solid contents of SiO₂, Al₂O₃, and TiO₂ were 0.8 g/L, 0.8 g/L, and 0.6 g/L, respectively, because the TiO₂ particles were easily agglomerated. The TiO₂ and Al₂O₃ nanoparticles have a high density, once agglomeration occurs, the enhancement factor will decrease rapidly.

![Figure 5](image)

Figure 5. Relationship between different particle enhancement factors and solid content.

3.2. Nanoparticle-MEA nanofluid absorption experiment

Figure 6 compares the enhancement factors of TiO₂-MEA nanofluids at three particle sizes. The enhancement factor of the nanofluid decreases as the particle size decreases, because the particle size decreases, the mass of the particles decreases, and the motion inertia decreases; In addition, the relative surface area of the particles increases, and the viscous resistance increases. Both of which cause the particle's ability to disturb the mass transfer boundary layer to be weakened.
Comparing figure 7, the absorption curves of the two amine solutions vary greatly. This is because the nitrogen atom in the MDEA structure is not directly connected to the hydrogen atom, and the zwitterion cannot be formed during the reaction with CO₂. Therefore, MDEA does not react directly with CO₂ like MEA. The higher the concentration of the organic amine, the greater the absorption of CO₂.

4. Conclusions
In this paper, a two-step method was used to prepare nanofluids. At the same time, enhancement factors were introduced to study the effect of nanofluids on mass transfer efficiency. The following conclusions were obtained: the nanofluid prepared by adding sodium polyacrylate has good stability and meets the experimental requirements; the enhancement effect of nanoparticles on MDEA/CO₂ absorption system is more obvious than MEA/CO₂ system; under the same solid content, TiO₂ have the largest enhancement factor, and SiO₂ has the smallest, even inhibiting effect; there is an optimum solid content, the value varies depending on the type of particle; in the particle size range used herein, the smaller the particle size, the smaller the enhancement factor; within the concentration range of the experimental study, the higher the concentration of the organic amine, the greater the absorption of CO₂.

Acknowledgments
The authors gratefully acknowledge the financial support from the Joint Funds of National Key R&D Program of China (2018YFB0604603), the National Natural Science Foundation of China (21536009), Key R & D Program of Shaanxi Province (2018ZDXM-GY-167), and Shaanxi provincial education department serves local special project (17JF029).

References
[1] Ramchandran, P.A., Sharma, M.M. (1969) Absorption with fast reaction in a slurry containing sparingly soluble fine particles. J. Chemical Engineering Science, 24(11):1681-1686.
[2] Kars, R.L., Best, R.J., Drinkenburg, A. A. H. (1979) The sorption of propane in slurries of active carbon in water. J. The Chemical Engineering Journal, 17(2): 201-210.
[3] Daungthongsuk, W., Wongwises, S. (2007) A critical review of convective heat transfer of nanofluids. J. Renewable & Sustainable Energy Reviews, 11(5): 797-817.
[4] Wang, X.Q., Mujumdar, A.S. (2007) Heat transfer characteristics of nanofluids: a review. J. International Journal of Thermal Sciences, 46(1): 1-19.
[5] Ma, H.B., Wilson, C., Borgmeyer, B., et al. (2006) Effect of nanofluid on the heat transport capability in an oscillating heat pipe. J. Applied Physics Letters, 88(14): 14-16.
[6] Choi, S.U.S., Eastman, J.A. (1995) Enhancing thermal conductivity of fluids with nanoparticles. J. Asme Fed: 231(1), 99-105.
[7] Gurav, P., Naik, S.S., Ansari, K., et al. (2014) Stable colloidal copper nanoparticles for a nanofluid: production and application. J. Colloids & Surfaces A Physicochemical & Engineering Aspects, 441(3): 589-597.
[8] Nguyen, C.T., Desgranges, F., Roy, G., et al. (2015) Temperature and particle-size dependent viscosity data for water-based nanofluids – hysteresis phenomenon. J. International Journal of Heat & Fluid Flow, 28(6): 1492-1506.
[9] Mojarrad, M.S., Keshavarz, A., Ziabasharhagh, M., et al. (2014) Experimental investigation on heat transfer enhancement of alumina/water and alumina/water–ethylene glycol nanofluids in thermally developing laminar flow. J. Experimental Thermal & Fluid Science, 53(2): 111-118.
[10] Safaei, M.R., Togun, H., Vafai, K., et al. (2014) Investigation of heat transfer enhancement in a forward-facing contracting channel using fmwcnt nanofluids. J. Numerical Heat Transfer Part A Applications, 66(12), 1321-1340.
[11] Dhuria, R., Dalia, V., Sunthar, P. (2017) Diffusiophoretic enhancement of mass transfer by nanofluids. J. Chemical Engineering Science, 176: 632-640.
[12] Kim, J.H., Jung, C.W., Yong, T.K. (2014) Mass transfer enhancement during CO₂ absorption process in methanol/Al₂O₃ nanofluids. J. International Journal of Heat & Mass Transfer, 76(6): 484-491.
[13] Wei, B., Zou, C., Li, X. (2017) Experimental investigation on stability and thermal conductivity of diathermic oil based TiO₂ nanofluids. J. International Journal of Heat & Mass Transfer, 104: 537-543.
[14] Yuan, Y., Li, X., Tu, J. (2017) The effects of nanoparticles on the lift force and drag force on bubbles in nanofluids: a two-fluid model study. J. International Journal of Thermal Sciences, 119: 1-8.
[15] Versteeg, G.F., Duck, L.A.J.V., Swaaij, W.P.M.V. (2010) Cheminform abstract: kinetics between CO₂ and alkanolamines both in aqueous and nonaqueous solutions. an overview. J. Cheminform, 28(6): no-no.