International Journal of Heat and Mass Transfer 127 (2018) 385–392

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

journal homepage: www.elsevier.com/locate/ijhmt

Effect of nanoparticles on the mass transfer process of removal of hydrogen sulfide in biogas by MDEA

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ARTICLE INFO

Article history:
Received 12 December 2017
Received in revised form 21 May 2018
Accepted 18 June 2018

Keywords:
Biogas
Hydrogen sulfide
MDEA
Cu nanoparticles
CuO nanoparticles
Mass transfer

ABSTRACT

In order to investigate the effect of Cu and CuO nanoparticles on the breakthrough time and mass transfer coefficient of removal of hydrogen sulfide from biogas by MDEA, the stable and homogenous MDEA-based Cu nanofluids and MDEA-based CuO nanofluids were prepared firstly. The viscosity of two types of nanofluids increased with concentrations but decreased with temperature increasing. Then absorption experiments indicated that the addition of nanoparticles could promote the removal of hydrogen sulfide from biogas by MDEA and the absorption efficiency of MDEA-based CuO nanofluids was better than that of MDEA-based Cu nanofluids. The maximum delay time of CuO nanofluids could be 380 min. The increase of temperature could slightly prolong the breakthrough time of the two types of nanofluids. But the desulfurization efficiency decreased greatly after the temperature exceeding 40 °C. The maximum mass transfer coefficient of nanofluids calculated by the double-contact column tower could be 17.75 mmol/s m^2 kPa at 0.06 vol% CuO nanofluids. All of these indicated that the favorable application prospect of CuO nanoparticles in desulfurization of biogas by MDEA.

1. Introduction

Biogas, as a renewable and clean energy, is produced by microbial action of organic matter. It contains a small amount of hydrogen sulfide (0.1–3 vol%) because of the existence of sulfoprotein [1–3]. Hydrogen sulfide, as a highly toxic substance, which can be detrimental to any biogas thermal or thermocatalytic conversion device and will pose a threat to humans and other organisms while it is released into the air [4]. On the other hand, this pollutant is highly undesirable in the energy transformation process, because it can be reverted into highly corrosive and environmentally hazardous sulfur dioxide (SO_2) and sulfuric acid (H_2SO_4). The removal of hydrogen sulfide is essential for any eventual utilization of biogas [5–7]. Some dry-process desulfurization technologies such as copper- and zinc-based active phases dispersed onto different supports had high removal efficiency, but the difficulty in regeneration is still a problem [8–10]. In the process of removing hydrogen sulfide by wet processes, the reaction process is difficult to be strengthened because of the mass transfer resistance at the gas-liquid interface. The conventional method of mass transfer enhancement is to promote mixture and turbulence of the phase body. But these methods of enhancing mass transfer are limited.

Ever since the new concept that nanofluids was first proposed by Choi et al. in 1995. Nanofluids as a new generation of promising materials, which had been applied in the fields such as the electronic equipment cooling [11–15], solar energy system [16], heat exchanger and machining process [17]. It is shown that the addition of fine particles in the adsorbent can enhance the mass transfer process. Dagaonkar [18] discovered that micron sized TiO_2 particles could enhance the physical absorption of pure CO_2 by water, hexadecane and sunflower oil. Kim [19,20] used 8% NH_3/H_2O solution as basefluid, the addition of nano-sized Cu, CuO and Al_2O_3 particles could highly improve the absorption performance of NH_3/H_2O solution, the enhancement could be greater with higher concentration. Pineda [21] studied that the effect of Al_2O_3, SiO_2 and TiO_2 nanoparticles on CO_2 absorption by CH_3OH, discovered that the addition of nanoparticles had no effect on absorption rate as the $R_{ew} < 17000$. However, in the counter-current flow, nanofluids showed better enhancement. Krishnamurthy [22] visualized dye diffusion in nanofluids. It was observed that dye diffused faster in nanofluids compared to that in water, with a peak enhancement at 0.5 vol%. Due to the superior mass transfer properties of nanofluids that had been studied by researchers [23–26], as far as we know, rarely was discovered to concern on application of nanofluids in absorption of hydrogen sulfide in biogas.

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https://doi.org/10.1016/j.ijheatmasstransfer.2018.06.091
0017-9310/

Nomenclature

Symbols

m	mass [g]
φ_v	volume fraction of nanofluids [%]
p_T	total pressure of gas phase [kPa]
L	diameter of liquid column [m]
A	gas-liquid contact area [m^2]
C_0	concentration of H_2S in the inlet [mg/m^3]
ρ	density [g/cm^3]
K_G	total mass transfer coefficient of gas phase [mmol/s m^2 kPa]
y	mole fraction of gaseous solute
Y	mole ratio
G_{N2}	flow rate of nitrogen [ml/min]
C	concentration of H_2S in the outlet [mg/m^3]
b	base fluid

Subscripts

p	nanoparticle
n	nanofluids

The goal of our present work is to test the effect of Cu and CuO nanoparticles on the mass transfer of H_2S in MDEA, and the corresponding mass transfer coefficients have been calculated to compare the absorption of H_2S in two different nanofluids. Characteristics of Cu nanoparticles and CuO nanoparticles such as the commercial availability, the high thermal conductive and chemical inertness, all contribute them to be promising materials [27–33]. In addition, MDEA as a kind of traditional excellent desulfurization solvent, it can highly select hydrogen sulfide in the purification of acidic gases. Therefore, the stable and homogeneous MDEA-based Cu nanofluids and MDEA-based CuO nanofluids were prepared. The stability and rheological behavior were studied firstly. Then the addition of nanoparticles, the type of particles and the effect of temperature on the absorption of hydrogen sulfide by MDEA were qualitatively studied by a bubble column apparatus. Gas-liquid double contact tower was used as a gas absorption device to simulate hydrogen sulfide absorption in biogas. A model of gas-liquid reaction was established and mass transfer coefficient was calculated.

2. Material and methods

2.1. 1Materials and preparation

In this paper, Cu nanoparticles (50 nm in diameter), CuO nanoparticles (50 nm in diameter) and pure MDEA were used. The Cu nanoparticles and CuO nanoparticles were procured from C.W. Nanotechnology Company (Shanghai, China), and their basic information are showed in Table 1. The base fluid MDEA and dispersant sodium dodecylsulphate (SDS) were gained from Kelong chemical reagent factory (Chengdu, China). In order to appraise the morphology of Cu nanoparticles and CuO nanoparticles, the transmission electron microscope (TEM) (HRTEM, TECNAI, Titan) was employed. The morphology for two types of particles was shown in Fig. 1(a) and (b).

To prepare the stable and homogeneous MDEA-based Cu and MDEA-based CuO nanofluids, the renowned two-step method was employed. The process for fabricating the two types of nanofluids was depicted as follows. Firstly, the well-prepared nanoparticles were suspended in the pure MDEA to obtain the desirable concentrations, which was mixed by a magnetic stirrer for 3 h. Then in order to obtain the stable and uniform nanofluids, an ultra-sonication homogenizer Sonifier 250 (Branson Ultrasonics, Danbury, USA) was employed to continuously disperse the mixture for 4 h. Before mixing the suspension, a small amount of sodium dodecylsulphate (SDS) as dispersant was added to guarantee the stability of nanofluids [34]. Since the stability of nanofluids decreases with increasing of nanoparticles concentrations, the maximum concentration of nanofluids in our experiments is 0.1 vol%. The whole steps were done at the constant temperature (293 K). The concentrations of nanofluids were counted by Eq. (1).

$$\varphi_v = \frac{m_n/\rho_n}{(m_n/\rho_n) + (m_b/\rho_b)} \tag{1}$$

2.2. Experimental apparatus

To evaluate the removal effect of hydrogen sulfide by nanofluids and obtain the breakthrough time of hydrogen sulfide, a laboratory test plant containing bubble column device was used, whose schematic flow diagram was shown in Fig. 2(a). The apparatus comprised a stainless steel column (15 mm ID, 650 mm in length), and it was immersed in a thermostatic bath, which was used to ensure a constant temperature during the absorption of hydrogen sulfide. Biogas containing hydrogen sulfide of certain concentration was prepared in a special gas cylinder, which was released by a pressure reducing valve and the gas flow rates was regulated by a mass flow controllers, then the gas was injected into the absorption column though a triple way valve after preheated. The off-gas was analyzed by means of a gas chromatograph (GC). Then the off-gas was discharged after being treated by the tail gas absorption bottle.

Fig. 2(b) showed the schematic flow diagram of laboratory test plant. A double-contact column tower meant that absorbent was injected into the tower from the bottom of the tower by pump, the simulated gas entered the tower through the bottom of the tower and contacted with the absorbent during the rising process, as the absorbent reaching the highest point, the counter-current contacted with the simulated gas during the descent process. The absorbent contacted twice with simulated gas in the process of rising and falling. The advantage was that the increase of the retention time of the absorption liquid in the reaction section,

Table 1
Basic information of Cu and CuO nanoparticles.

Material	Average diameter	Surface area	Bulk density	Thermal conductivity
Cu nanoparticles	50 nm	68.35 m^2/g	2.103 g/cm^3	380 W/(m K)
CuO nanoparticles	50 nm	59.46 m^2/g	2.405 g/cm^3	86 W/(m K)