Effect of reactor geometry on aqueous ammonia-based carbon dioxide capture in bubble column reactors

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A B S T R A C T

Capture of carbon dioxide (CO_2) from combustion flue gas by aqueous ammonia has been demonstrated as an effective and promising technology. To examine the effect of reactor geometry on ammonia-based CO_2 capture performance, a series of bubble column reactors with same volume of working liquid but varied geometry (liquid height-to-diameter ratios $H/D = 0.93$, 2.04 and 3.98) were designed to investigate CO_2 capture efficiency with ammonia under different reaction conditions. It is found that reactor geometry characterized by liquid height-to-diameter ratio plays an important role in CO_2 capture efficiency as it is associated with gas holdup time in reactors. CO_2 capture efficiency increases as liquid height-to-diameter ratio increases. Under the same experimental conditions, the maximum CO_2 capture efficiency can increase by up to 7%. Besides, CO_2 capture efficiency has positive correlation with the ammonia concentration and reaction temperature whereas has negative correlation with the CO_2 inlet concentration and flue gas flowrate.

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1. Introduction

Carbon dioxide (CO_2) has been regarded as one of most important greenhouse gases (GHGs) (Georgios and Paul, 2009). Anthropogenic CO_2 emissions from fossil fuel utilization especially from coal combustion make a significant contribution to global CO_2 emission (Pachauri and Reisinger, 2007). Effective capture of CO_2 relates to several factors, e.g., the high concentration (10–20%, v/v) of CO_2 in flue gas, the high flowrate of flue gas, coexisted toxic pollutants such as SO_2, NO_x, HCl and trace metals (Hg, Se, As, etc.). To effectively reduce the post-combustion CO_2 emission, the stable, safe and environmentally acceptable post-combustion CO_2 capture technologies are required besides improving energy efficiency and developing renewable energies (Kannicha and Bouallow, 2007).

Different methods have been intensively investigated for CO_2 capture from combustion flue gas, including chemical or physical adsorption, membranes separation (Mohamed et al., 2008), cryogenics separation (Chris and Hendriks, 1995), etc. Chemical looping combustion (CLC) (Mattisson et al., 2001) and biotechnology (Ho et al., 2011) were also considered as effective ways to reduce CO_2 emission. So far chemical absorption technology seems to be the most suitable technology to reduce CO_2 emission at industrial application level due to its obvious advantages, e.g., high

performance and mature technology (Zhao et al., 2011; Lin and Chen, 2007; Versteeg et al., 1996). The key point of chemical absorption technology lies in the absorbent. Over the past several decades, alcohol amines, including Monoethanolamine (MEA) (Alie et al., 2005; Mamun et al., 2007), diethanolamine (DEA), triethanolamine (TEA) and *N*-methyldiethanolamine (MDEA) (Aroonwilas and Veawab, 2004; Pacheco et al., 2000), are commonly used as the absorbent. However, they usually suffer the disadvantages of high energy requirement for regeneration, easy oxidization/degradation by SO_2 and O_2 in flue gas and system corrosion (Yan et al., 2006), although they have better technical and economic feasibility than strong alkalines and their salt solutions (e.g., KOH, NaOH and Na_2CO_3). The choice of the cost-effective and high-performance absorbent is still a very open and interesting question. Future research efforts should be directed toward developing better solvents for the removal of CO_2 with high CO_2 loading capacity and low regeneration energy (Wolsky et al., 1994; Resnik et al., 2004). Aqueous ammonia ($NH_3 \cdot H_2O$) was demonstrated to be a very good alternative absorbent (Zhao et al., 2012). Besides the general advantages such as high absorption efficiency, high absorption capacity, low energy requirement for absorbent regeneration and wide distribution of resources (Bai and Yeh, 1997; Yeh and Bai, 1999; Yeh et al., 2005; Niu et al., 2010a, 2010b), aqueous ammonia could simultaneously remove SO_2, NO_x and oxidized mercury. Furthermore, the by-products, amine salts produced during the reaction of ammonia with CO_2, SO_2 and NO_x, can be used as fertilizer for soil improvement. As a promising approach and technology,

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post-combustion CO_2 capture by aqueous ammonia is receiving increasing attention (Dong et al., 2007; Yeh et al., 2005) and even had pilot scale applications (Kozak et al., 2009; Bollinger et al., 2010).

The understanding of fundamental mechanism of ammonia-based CO_2 capture is critical for its industrial and engineering application. Previously reports particularly focused on NH_3–CO_2 process chemistry and reaction conditions (Zhao et al., 2012). Specifically, the dissolution and absorption of CO_2 into aqueous ammonia is accompanied by a series of complex physicochemical processes which are related to the concentration, temperature, pressure and turbulent conditions (Edwards et al., 1975, 1978; Göppert and Maurer, 1988; Mishima et al., 1989; Bernardis et al., 1989; Kurz et al., 1995; Hassan and Amir, 2005; Pazuki et al., 2006). The major chemical reactions, reaction products and reaction kinetics are listed in Table 1. Actually, CO_2–NH_3–H_2O chemical reaction consists of a series of multi-step and reversible reactions (Brooks and Audrieth, 1946; Hatch and Pigford, 1962; Koutinas et al., 1983; Bai and Yeh, 1997; Yeh and Bai, 1999; Liu et al., 2009). The overall reaction can be simply represented by Eq. (6). According to different analytical methods, it was also demonstrated that NH_4HCO_3 should be the primary reaction product as the forward reaction of CO_2–NH_3–H_2O system is dominant at normal pressure and temperature (Yeh and Bai, 1999). Furthermore, the CO_2–NH_3–H_2O reaction kinetic parameter can be expressed as the form of Arrhenius equation based on the single equation reaction mechanism.

In addition to the process chemistry, it has been demonstrated that ammonia-based CO_2 capture performance was strongly affected by reaction conditions and reactor configurations (Cheng et al., 2006; Versteeg et al., 1996; Alie et al., 2005; Mamun et al., 2007; Aroonwilas and Veawab, 2004; Pacheco et al., 2000). Bubble column reactors (BCR), as one of important compact multiphase reactors with high heat and mass transfer rates and low operation and maintenance costs (Kantarci et al., 2005), has been widely used in a variety of chemical and biochemical gas-liquid reaction systems (Shah et al., 1982; Deckwer and Schumpe, 1993). During the past decades, fundamental researches in bubble column reactors have increased considerably (Kantarci et al., 2005). In spite of the relatively simple geometry, complex multiphase hydrodynamics, transport characteristics and reaction processes make bubble column reactors difficult to achieve accurate and reliable design. Factors including parameters of gas and liquid physicochemical properties, parameters of operating conditions and parameters of geometry and configuration influence the performance of BCR significantly. Bai and Yeh (1997) and Yeh and Bai (1999) investigated the ammonia-based CO_2 capture in a bubble column reactor. Their results indicated that the maximum CO_2 capture efficiency by aqueous ammonia absorbent was as high as 95% and the CO_2 loading capacity approached to 1.20 g CO_2/g NH_3. Although the CO_2 capture performance in a BCR has been preliminarily examined, the relationship between structural or geometrical parameters of BCR and CO_2 capture performance by aqueous ammonia has not yet been reported.

In the present work, a series of BCRs with same volume of working liquid but varied geometry were designed to examine its effect on CO_2 capture efficiency based on aqueous ammonia method. As the liquid volume in reactor keeps constant, the height of the liquid is inversely proportional to the square of inner diameter of reactor (also diameter of liquid). To characterize the BCR geometry with fixed solvent volume, an important design and structural parameter liquid height-to-diameter ratio (H/D) was used since it is associated with both the reactor shape and gas holdup time (retention time) (Wu et al., 2001). The unsteady and maximum CO_2 capture efficiencies were compared and evaluated under varied reaction conditions, including the ammonia concentration, CO_2 inlet concentration, flue gas flowrate and reaction temperature.

2. Experiment and method

2.1. Experimental setup and conditions

The schematic diagram of the experimental system is illustrated in Fig. 1. Simulated flue gas consisted of varied concentration of CO_2 balanced with N_2 was aerated into the bubble column reactor. The bubble column reactors with bubble size of 1.5 mm were designed with varied geometry (characterized with $H/D = 0.93$, 2.04 and 3.98), as shown in Fig. 2. In this test, 200 ml (work volume) aqueous ammonia with varied concentrations was used as solvent contained in reactors. They could be diluted by ammonium hydroxide solutions (analytical reagent, 28%, w/w) to obtain desired ammonia concentrations. Gas flow was adjusted with a gas rotameter. The reaction temperatures were controlled by a constant temperature water bath. Gas washing bottle with sulfuric acid solution and gas dryer were used to prevent the volatilized ammonia and water vapor from entering into the simulated flue gas after reaction, respectively. Finally, CO_2 concentration was measured using the online infrared CO_2 analyzer (GXH-3010E1).

In the experiments, the reaction (operating) parameters including ammonia concentration, CO_2 inlet concentration, total flue gas flowrate and reaction temperature were systematically varied to

Table 1
Process chemistry of NH_3–CO_2 reaction.

Item	Specification		References
Reaction mechanism	Substages:		Brooks and Audrieth (1946), Hatch and Pigford (1962), Koutinas et al. (1983), Bai and Yeh (1997), Yeh and Bai (1999), Liu et al. (2009)
	$2NH_3 + CO_2 \rightleftharpoons NH_2COONH_4$	(1)	
	$NH_2COONH_4 + H_2O \rightleftharpoons NH_4HCO_3 + NH_3$	(2)	
	$NH_3 + H_2O \rightleftharpoons NH_4OH$	(3)	
	$NH_4HCO_3 + NH_4OH \rightleftharpoons (NH_4)_2CO_3 + H_2O$	(4)	
	$(NH_4)_2CO_3 + CO_2 + H_2O \rightleftharpoons 2NH_4HCO_3$	(5)	
	Overall:		
	$NH_3 + CO_2 + H_2O \rightarrow NH_4HCO_3$	(6)	
Reaction products	Early stage: NH_2COO^-		Holmes II et al. (1998), Mani (2006), Meng et al. (2005), Zhang et al. (2008), Lin (2008), Park et al. (2008), Zhao et al. (2011)
	Last stage: HCO_3^-		
	Primary product: NH_4HCO_3		
Reaction kinetics	$\ln K = \ln A - \dfrac{E_a}{RT}$	(7)	Andrew (1954), Pinsen et al. (1956), Hsu (2003), Diao et al. (2004), Rivera-Tinoco and Bouallou (2010)
	where $\ln A = 9.4867$–25.6278, $E_a = 26.730$–48.529 kJ/mol ($T = 0$–$50\,°C$)		