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Enriching blast furnace gas by removing carbon dioxide

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Abstract

Blast furnace gas (BF gas) produced in the iron making process is an essential energy resource for a steel making work. As compared with coke oven gas, the caloric value of BF gas is too low to be used alone as fuel in hot stove because of its high concentrations of carbon dioxide and nitrogen. If the carbon dioxide in BF gas could be captured efficiently, it would meet the increasing need of high caloric BF gas, and develop methods to reusing and/or recycling the separated carbon dioxide further. Focused on this, investigations were done with simple evaluation on possible methods of removing carbon dioxide from BF gas and basic experiments on carbon dioxide capture by chemical absorption. The experimental results showed that in 100 minutes, the maximum absorbed doses of carbon dioxide reached 20 g/100 g with ionic liquid as absorbent.

Key words: carbon dioxide capture; BF gas; absorption; PSA; ionic liquid

Introduction

In recent decades, the climate warming caused by over exhaust of CO_2 has become one of the most concern issues. On the other hand, both CO and CO_2 are valuable carbon resources in the nature, thus the capture, storage and recycling of CO_2 are significant (Shi et al., 2006).

Nowadays, China has become the biggest producer in iron and steel materials in the world. Much attention must be paid to an environmentally benign steel making process to decrease the pollution of the atmosphere surroundings. In the iron making process of blast furnace, a large quantity of blast furnace gas (BF gas) which is a by-product will be inevitably produced. Due to high concentration of CO_2 and nitrogen and feature of low caloric value, BF gas is limited in use in some extent. Because its combustible component is only about 18%–25%, BF gas is a kind of low caloric fuel gas. For example, by using BF gas as fuel of hot stove alone, it is impossible to get the high temperature of hot blast over 1473 K (Zhang et al., 1999). Thus certain proportion coke oven gas with high caloric has to be used and mixed with BF gas, or pre-heating process to the fuel gas and fuel air have to be adopted. Then, in the combustion process of hot stove, the original CO_2 in the BF gas, without any positive effect, only absorbs physical heat and consumes energy. It is important to promote a deep investigation on capturing CO_2 from BF gas and hence concentrating BF gas. In European Union, an ULCOS steel making system is under construction in which separation of CO_2 is also considered (Birat and Hanrot, 2006).

Separation of CO_2 can be mainly divided into four types, distillation, absorption, film separation and adsorption (Meisen and Shuai, 1997; Douglas and Costas, 2005). Distillation at low temperature is suitable for the gas of CO_2 concentration above 60% but it is unfit for BF gas because no CO_2 concentration in BF gas is higher than 25%. In spite of advantages of simple, low energy consumption, film separation needs pretreatment to virgin gas which is difficult to BF gas for its huge amount. Since its commercial application in 1986, pressure swing adsorption (PSA) has been developed well for the cycle process with advantages of low consumption of energy, simple in the flow and easy to realize automatic operation. PSA cycle has some disadvantages such as pressure drop and small processing capacity (Choi et al., 2003; Rege et al., 2005). According to the feature of BF gas with large quantity and low concentration of CO_2, absorption was chosen in this study.

1 Materials and methods

1.1 Materials used in syntheses of absorbents

The main chemical reagents used in these experiments are listed in **Table 1**.

Using amines and organic acids, twelve kinds of ironic liquids were synthesized through neutral reactions follow-

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Table 1 Main chemical reagents in the work

Name	Purity	Molecular formula
Methanoic acid	≥ 88%	HCOOH
Acetic acid	≥ 99.5%	CH_3COOH
Propanoic acid	≥ 99.0%	CH_3CH_2COOH
Lactic acid	≥85.0%	$C_3H_6O_3$
Ethylenediamine	≥ 99.0%	$H_2NCH_2CH_2NH_2$
DETA	≥ 98.0%	$C_4H_{13}N_3$
Triethylenetetramine	≥ 98.0%	$C_6H_{16}N_4$
Ethyl acetate	100.0%	$CH_3COOC_3H_5$
Diethanol amine	≥ 99%	$C_4H_{11}NO_2$
triethanola mine	≥ 99%	$C_6H_{15}O_3$
N-methylimidazole	≥ 99%	$C_4H_6N_2$
Bromobutane	≥ 99%	C_4H_9Br

ing the mechanism below.

$$H_2N\text{-}R_1\text{-}NH_2 + R_2COOH \Leftrightarrow [H_2N\text{-}R_1\text{-}NH_3]^+ + [R_2COO]^- \quad (1)$$

During the syntheses processes, the reactions are exothermic and even a lot of white smoke were found.

An infra-red spectrogram of synthesized product–triethylene tetramine formate in this work is shown in **Fig.**

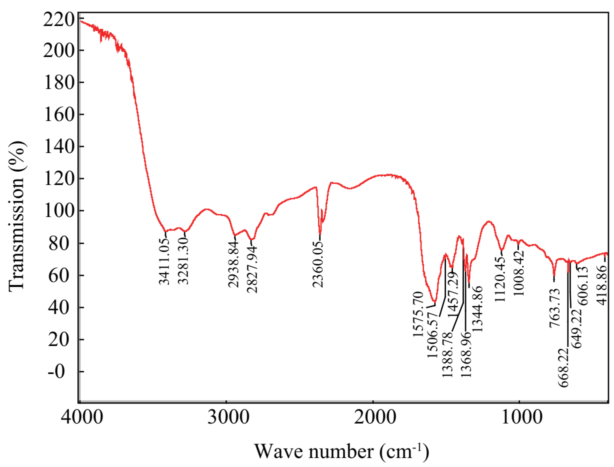

Fig. 1 IR spectrogram of the synthesized product.

1. Form the spectrogram, some characteristic functional group such as COO^-, $\text{-}NH_3^+$, $\text{-}CH_2$ and $\text{-}NH_2$ can been found, which can prove that the synthesized product is an ironic liquid.

1.2 Experimental method of absorption

Weighing method was adopted in the experiments of absorption to carbon dioxide, which means the weights of absorbents in the absorption must be measured in every 10 min. The absorptive experiments were done at 298 K.

2 Results

2.1 Alkanolamines aqueous liquids as the absorbents

The experimental results of absorption to CO_2 of Di-ethanolamine (DEA) and Triethylolamine (TEA) aqueous liquids are showed in **Fig. 2**.

2.2 Aqueous ironic liquids as the absorbents

Ironic liquids synthesized in this work were used in the absorptive experiments of CO_2 at normal temperature (25°C). Parts of experimental results of aqueous solutions of ionic liquids are showed in **Fig. 3**.

3 Discussion

3.1 Possibility PSA cycle

PSA is a kind of adsorption cycle process, in which at certain temperature, the same component can be adsorbed by the adsorbent under a higher partial pressure, and the rest components are expelled from the tower, then at a lower partial pressure even in vacuum, the adsorbed component is desorbed, meanwhile the adsorbent will be regenerated (Fukunaga et al., 1968; Gomes and Yee, 2002; Takamura et al., 2001). In addition to pressurization, feed, countercurrent depressurization and purge four original steps, new operation steps such as repressurization, equal-

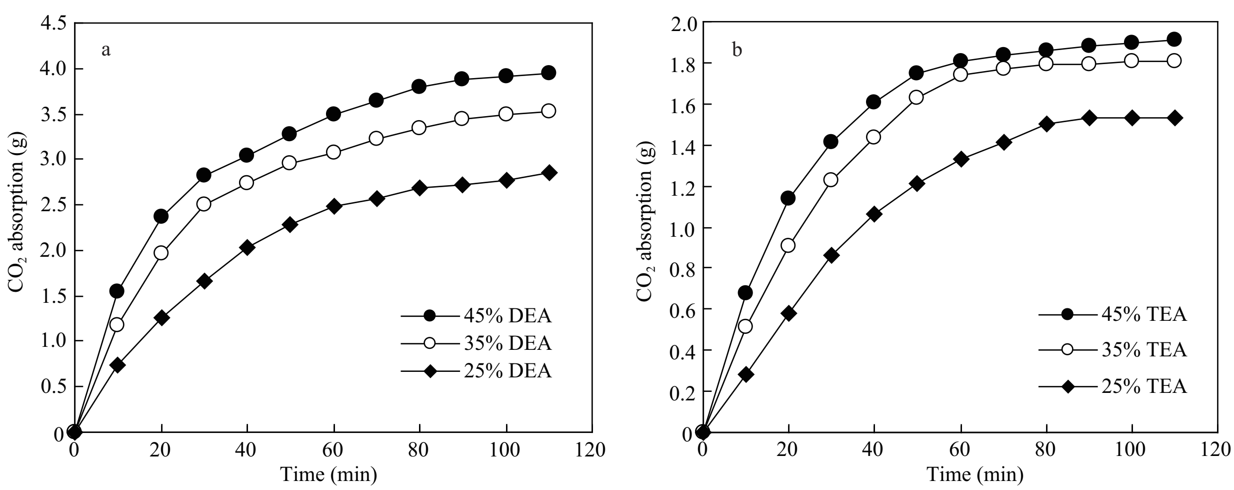

Fig. 2 CO_2 absorptive abilities by use of DEA aqueous liquids (a) and TEA aqueous liquids (b) at 25°C on 100 g absorbent.

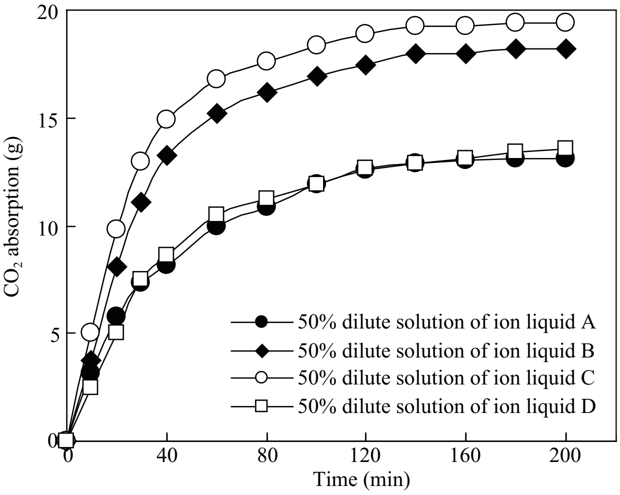

Fig. 3 CO_2 absorption curves by use of dilute aqueous solutions of ion liquids synthesized at 25°C over 100 g absorbent.

ization, co-current depressurization and reflux were also put forward (Anderson and Newell, 2004; Park et al., 2002).

According to the principle of PSA cycle, a minimum pressure differential of 100 k Pa is required for the cycle working, but small parts of blast furnaces with high pressure operation can meet the requirement nearby 2000. BF gas is produced largely in quantity, it needs large scale equipment of PSA cycle to process, and the waste gas emission will cause secondary contamination (Zhang et al., 2000). Nevertheless, PSA cycle is good alternatives for CO capture in BF gas ever though there still are some other obstacles.

3.2 Possibility of alkanolamines aqueous liquids as the absorbents

With advantages of good stability and low energy consumption, alkanolamines aqueous liquids as conventional absorbents have successfully been used in absorption SO_2 and CO_2 from natural gas, coke oven gas and other fuel gases in chemical industry (Huang et al., 2008; Abdelbaki, 2007; Li et al., 2009). Since piperazine was adopted as the activator of N-methyldiethanolamine for absorbing CO_2 (Wang, 2008), many activated alkanolamines aqueous liquids have been developed and hydroxyl ammonium ionic liquids have been synthesized (He et al., 2009; Yuan et al., 2007; Kurnia et al., 2009)

The model of CO_2 absorbed by alkanolamines aqueous liquids can be expressed as:

$$CO_2 + RNH_2 = RNH_2^+ COO^- \quad (2)$$

$$RNH_2^+ COO^- + B = RNHCOO^- + BH^+ \quad (3)$$

here B is the amine molecules in the liquid mainly.

The regeneration process and desorption can be realized by thermal decomposition as follows:

$$RNHCOO^- + H_2O = CO_2 + RNH_2 + OH^- \quad (4)$$

Regeneration is an important factor to the use of the alkanolamines aqueous liquids widely, from which it can be seen the order of regeneration: AMP > MDEA > DETA > DEA > MEA (Cai, 2009).

To a continuous production process like steel making, pipe line corrosion is a fatal weakness. It is uncertain whether the pipes and other BF gas equipment will be corroded in the weak alkaline medium of alkanolamines aqueous liquids, but there is possibility of steel corrosion.

Form results of this work, the absorptive loads are not higher than 5 g/100 g absorbents) when alkanolamines aqueous liquids were used as the absorbents. In real operation in blast furnace, consumption of energy of cycles caused by relatively small absorptive load for CO_2 is another weakness.

3.3 Possibility of aqueous ionic liquids as the absorbents

As to CO_2, Bates et al. (2002), who had synthesized the functionalization ionic liquid with functional groups $-NH_2$ (TSILS), found that the ionic liquid containing functional groups $-NH_2$ is much better than that ionic liquid without this functional group in the aspect of adsorbing CO_2. At normal temperature and pressure, this CO_2 adsorption rate of ionic liquid with functional groups $-NH_2$ can reach 7.4% (mass fraction). The study results show that the functionalization ionic liquid is expected to replace the current industry and some organic solvents using for separation and removal of CO_2.

It has been proved that CO_2 in [APBIM] [BF_4] is a kind of chemical absorption, [APBIM] [BF_4]-NH_2 and CO_2 reacted to form the carbonate of ammonium by FT-IR and CNMR spectra (Tang et al., 2005).

A series of amino acid ionic liquids have been synthesized in Zhang's work. Because of the high viscosity of the ionic liquid he synthesized, it was coated on the surface of porous silica gel, forming a film on the surface and the experiment was cycled for 4 times. Comparing with the absorption that CO_2 is directly put into ionic liquids, more rapid absorption, stability as well as reversible absorption - desorption process and recycled absorbent were found in this experimental method of surface coated (Zhang et al., 2006).

It was also found in this experiment that the viscosities of most ionic liquids synthesized in this work are too high to be used as absorbents alone. In order to realize the adsorption of CO_2 with synthesized ionic liquids, aqueous solutions of ironic liquids were made. The experimental results showed that aqueous solutions of ironic liquids are much better than pure ionic liquids on absorptive loads of CO_2. A comparison on absorptive loads between

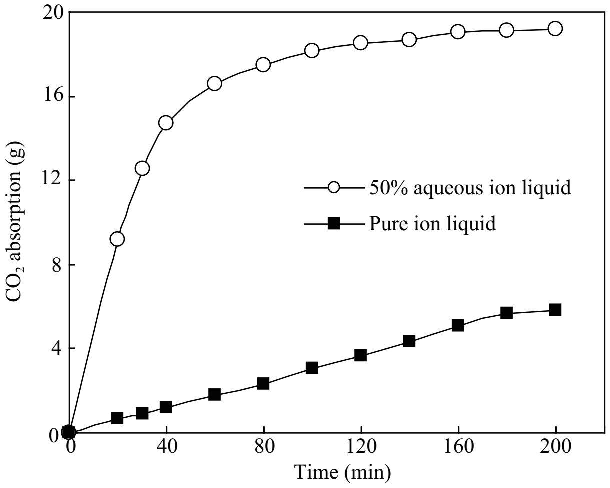

Fig. 4 Comparison of CO_2 absorption by use of pure ionic liquid and its aqueous dilute solution at 25°C over 100 g adsorbent.

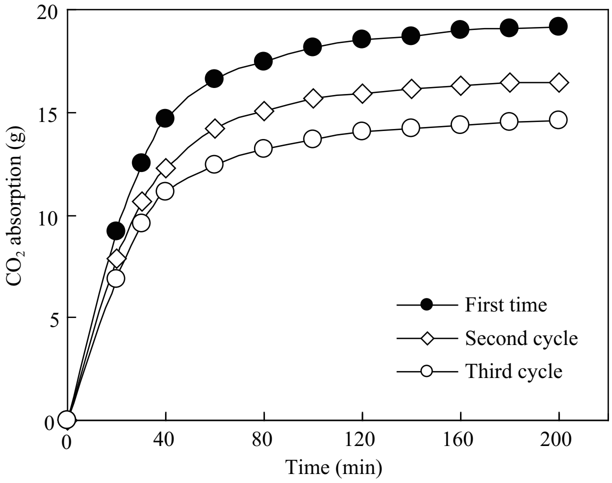

Fig. 5 CO_2 absorptive capacities in different regeneration cycles of ionic liquid A synthesized at 25°C over 100 g adsorbent.

pure ionic liquid and its aqueous solution is showed in **Fig. 4**. Moreover, In contrast to less than 5 g CO_2/100 g absorbents in alkanolamines aqueous liquids absorption, the absorptive loads of aqueous solutions of ironic liquids are over 10 g CO_2/100 g absorbents, the best result is about 19 g CO_2/100 g absorbent.

Regeneration is vital to putting ionic liquids into steel making process for capturing CO_2. A group of experiments for regeneration of ionic liquids were done. It was found that the CO_2 absorptive abilities of each ionic liquid decrease while using the recovery ionic liquids in their second and third cycle. The results in this condition indicate that regeneration rates are 90% in the second cycle and 88% in the third cycle. The CO_2 absorptive abilities of aqueous ionic liquid A in different cycling absorption are showed in **Fig. 5**.

Comparing the above methods for separating CO_2 in steel making process, chemical absorption with ionic liquid is the most promising. In spite of advantages in ionic liquid absorption, there are difficulties to be overcome with the aim that ideal ionic liquid can be easy synthesized with high efficiency and low price. It is expected the ionic liquids can absorb CO_2 steadily and recycle with high regeneration ratio at an average temperature of BF gas (about 350 K), and should not cause second contamination to the surroundings.

4 Conclusions

BF gas is large in quantity, according to the feature of PSA process, it needs large scale equipment, and the waste gas in the PSA process should be treated well.

Alkanolamines aqueous liquids and with their advantages of low price and easy to synthesize are good in absorption to CO_2 and have been used in chemical fields, the experiment results showed that the absorptive loads are not higher than 5 g/100 g absorbents, so it needs large quantities of liquids for circulation and energy consumption in the operation if used them in blast furnace. Moreover, the weaknesses of alkalinity-bearing and corrosion to the steel reactor in alkanolamines aqueous liquid should not be underestimated.

The experiments of ionic liquid absorption showed that pure ionic liquids absorptive abilities are limited due to their high viscosities. In this work, it is found that the absorptive abilities of aqueous ionic liquids can reach 19 g CO_2/100 g absorbent which is much higher than that in the absorption of alkanolamines aqueous liquids. The regeneration ratios in the aqueous solutions are about 90% in the second cycle and 88% in the third cycle.

Analyses indicate that the three ways of separating CO_2 from BF gas, there are advantages and weaknesses for each method. Comparatively, absorption of ionic liquids is more promising.

Acknowledgments

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