Poly-amino-based ionic liquids coupled with semi-coke for biogas upgrading

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Abstract—Poly-amino-based ionic liquid (IL) [TETAH][BF4] was mixed with sodium hydroxide solution for CO2 separation from biogas in a spray scrubber packed with modified semi-coke. A CO2 absorption capacity of 0.92mol was achieved when controlling the outlet CO2 concentration below 3 vol%. The porous structure of semi-coke contributed to improving CO2 absorption. Nitric acid oxidation and heat treatment could increase the specific surface area, enlarge the intrinsic pores and develop more micropores. Semi-coke firstly oxidized by nitric acid and then with heat treatment could not only exhibit higher specific surface area and more porous structure, but also show less degree of graphitization, which was suggested as possible to increase the reactivity to CO2. It was assumed that the absorption system in this research showed promising application in CO2 separation from biogas as well as waste treatment.

1. Introduction
To achieve the carbon peak and neutrality targets, increasing the share of non-fossil energy consumption is vital important. Biogas, one of the promising renewable energy has attracted worldwide interest as its potential applications in heating, electricity generation and as vehicle fuel [1-2]. However, the applications would be limited unless the carbon dioxide content is significantly reduced. Different technologies for CO2 separation from biogas have developed, and each has its own advantages and disadvantages. For example, traditional approach such as aqueous amine solutions have the advantages of high reactivity, high surface tension, and low methane solubility, while show disadvantages such as equipment corrosion, high solvent loss, degradation and insufficient CO2 capture capacity[3]. As a result, researchers are still looking for technology-effective and cost-effective methods for CO2 separation.

Ionic liquids (ILs), the organic salts mainly composed of organic cations and inorganic/organic anions, have been considered as potential alternative solvents for CO2 capture. Comparing to alkanolamines, the advantages of applying ILs in biogas upgrading should be appraised on the less corrosivity, high stability before and after absorption as well as the negligible vapor pressure, which would prevent the absorbent loss and the discharge of volatile chemicals [4]. A great many researches have been carried out so as to increase the CO2 absorption capacity and absorption rate of ILs. Functionalized ILs grafted amino-group into cation or anion have found to be effective absorbents for CO2 capture due to the greatly improved capacity and velocity of CO2 absorption[5]. However, the competitiveness of applying ILs in large-scale biogas upgrading is limited by the high viscosities and high production costs[6]. The viscosities, originated from the strong interactions between their constituent ions, are even much higher for amine functionalized ILs. As a result, methods of blending...
amine functionalized ILs with commercially available solvents such as water, amine, ethanol and other non-ionic surfactants are widely adopted. Research results indicate that the mixtures can retain the desired capture effect of ILs, also, keep the viscosity and cost relatively low.

Besides solvents, many kinds of absorption materials were adopted for efficiently applying ILs in industrial manufacture of CO₂ separation. But most of were limited by the excessive price in commercial application.

Semi-coke, a product of coal pyrolysis at a relatively low temperature (873-973 K), has received a wide attention due to the low cost, well-developed porous structure and plentiful surface functional groups. The main ingredients of semi-cokes are carbon, ash and volatile compounds. The absorption activity can be improved by removing ash and volatile, changing composition of functional groups and altering the structure of carbon materials through modification. Although the surface area of semi-cokes is lower than activated carbon, the relatively higher mechanical strength of semi-coke facilitates the upgraded scale application.

In this paper, the poly-amino-based ILs selected could be easily synthesized by neutralization of polyamine and inorganic acid. The objective of this research is to determine the feasibility of using the ILs/NaOH solution as potential absorbent for biogas upgrading in a packed spray system. The absorption effects and the influencing factors of this dual system have rarely been reported. Semi-coke modified by nitric acid and heating treatment was used as structured materials to enhance the absorption effect. The effects of operational conditions such as mole ratio, absorbent concentration and semi-coke on CO₂ capture were investigated. The potential synergism for CO₂ absorption by poly-amino-based ILs/NaOH solution and semi-coke was analyzed.

2. Materials and methods

2.1 Materials
The [TETAH][BF₄] (purity>98%) was self-made following the literature [7]. Nitric acid (HNO₃, purity 68 %) and sodium hydroxide (NaOH, purity>99.5%) were supplied by Sinopharm Chemical Reagent Co., LTD. The simulated biogas consisted of 40 vol% CO₂ and 55 vol% CH₄ was obtained from Wuhan Specialty Gases Co., LTD.

The raw materials were milled and sieved to obtain fragments about 5-8 mm for the experiment. For the preparation of SN600, the sample was firstly washed with water to remove small particles and ash from the surface. And then sample was immersed in 45 wt% nitric acid and boiled for 2 hours at 363 K. Following that, the sample was treated with a tube furnace at 873 K for 2 hours under the atmosphere of N₂. For the preparation of S600N, the sample was firstly treated with a tube furnace at 873 K for 2 hours under the atmosphere of N₂, and then immersed in 45 wt% nitric acid and boiled for 2 hours at 363 K.

2.2 Experimental setup and operation
The absorption of CO₂ was carried out in a laboratory-scale spray scrubber packed with 350 mm semi-coke. As schematically shown in Fig.1, the scrubber consisted of a cylindrical perspex tower of 1000 mm in height and 80 mm in diameter. An atomizer with orifice diameter of 1 mm and spray angle of 0-100° was fixed at the upper part of the scrubber and the mean diameter of the spray was 20-30 μm when the pressure of the mechanical diaphragm metering pump was 0.5-1.0 MPa. The CH₄/CO₂ mixture was introduced from the bottom of the tower while the NaOH/ILs solution was sprayed from the top to form a counter-current flow. The mixed gas and the NaOH/ILs solution were heated to the designated temperatures before being introduced into the scrubber, and the temperatures were continuously monitored. The flow rates and accumulated volume of the gas were measured using a soap-film flow meter (Agilent Technologies Co. LTD.). The CO₂ concentrations were measured by a Biogas 5000 analyzer (Geotech, England).
Raman spectra of semi-coke were obtained using the Raman spectroscopy (LabRAM HR800) with a 532 nm, 0.05 mW laser over two cycles of exposure (5 s for each cycle). Morphologies of semi-coke samples were studied with an SEM (JSM-5610LV, JEOL Co., Japan) at the accelerating voltage of 25 kV.

The CO2 absorption capacity of the NaOH/ILs solution was calculated by the following equations:

\[
n_{\text{CO2}} = \left( \frac{C_{\text{in}} \times Q_{\text{in}} \times \pi \times D^2}{2 \times V_{\text{mol}}} \right) \times \frac{C_{\text{out}} - C_{\text{in}}}{C_{\text{in}}} \times \frac{D^2}{4} \times \frac{1}{V_{\text{mol}}} \times V_{\text{mol}} = \frac{P_0}{P} \times \frac{T}{T_0} \times V_0
\]

where \( n_{\text{CO2}} \) was the CO2 absorption capacity (mol CO2/mol absorbent), \( C_{\text{in}} \) and \( C_{\text{out}} \) were the concentration of CO2 in inlet and outlet gas (vol%), \( C_{\text{in}} \) was the volumetric concentration of CO2 in the spray scrubber before absorption, \( C_{\text{ab}} \) was the absorbent concentration in solution (mol/L), \( t \) was the absorption time (min), \( Q_{\text{in}} \) and \( Q_{\text{out}} \) were the flow rate of inlet and exit gas (L/min), \( D \) was the diameter of the spray scrubber, \( V \) was the volume of the solution, \( V_{\text{mol}} \) was the mole volume of gas at the temperature of \( T \) and pressure of \( P \), \( T_0 \) was 273 K, \( P_0 \) was 1 bar, \( V_0 \) was 22.4 L/mol. We supposed that the concentration of CO2 homogeneously varied along the direction of height when calculating the amount of CO2 in the spray scrubber.

| Experimental conditions | Expt.3.1 | Expt.3.2 | Expt.3.3 |
|-------------------------|---------|---------|---------|
| Temperature(K)          | 288     | 288     | 288     |
| Mole ratio of NaOH to ILs| 4:1-1:4 | 4:1     | 4:1     |
| Liquid-to-gas ratio     | 1:3     | 1:3     | 1:3     |
| Volume of the NaOH/ILs solution(L) | 3       | 3       | 3       |
| liquid flow rate(L/min) | 0.3     | 0.3     | 0.3     |
| Concentration of the absorbent(mol/L) | 0.4     | 0.2-0.5 | 0.4     |

3. Test Results and Discussions

3.1. The effect of IL mole ratio on CO2 absorption

Fig. 2(a) shows the effect of mole ratio on CO2 absorption. With the mole percentage of IL rising from 0 to 20 %, the CO2 absorption mole ratio increased from 0.44 to 0.54 while controlling the outlet CO2 concentration below 3 %, by which point the quality of the outlet gas could meet the standards of compressed natural gas as vehicle fuel (GB 18047-2000) in China. With the percentage of IL rose up
to 40%, the CO₂ capture capacity began to decrease, and reduced to 0.34 when the percentage of IL was 80%. Accordingly, the time to obtain qualified natural gas showed the same trend. It was revealed that the mixture of a small amount of IL and the bulk of sodium hydroxide solution could improve the CO₂ capture capacity because of the high absorption capacity of IL. However, this promotion may be limited by the high viscosity of IL and the reaction product when the percentage of IL continued to increase. Such high viscosity hindered the diffusion of CO₂ into the bulk liquid phase and seriously reduced the mass transfer rate. Further, the porous structure of semi-coke would be jammed by the reaction product that not timely diffused and formed foam layers. Therefore, the CO₂ capture ability experienced a reduction.

3.2 The effect of absorbent concentration on CO₂ absorption

Fig. 2(b) shows the effect of absorbent concentration on CO₂ absorption. When the absorbent concentration increased from 0.2 to 0.5 mol/L, the time of obtaining qualified natural gas with 3 L solution increased from 24 minutes to 50 minutes. However, the CO₂ absorption mole ratio was obviously decreased, which varied from 0.65 to 0.54 as the concentration increased to 0.3 mol/L when controlling the outlet CO₂ concentration below 3%, and not varied much as it continued to rise. The possible reasons could be explained as: on the one hand, sodium hydroxide exhibited higher reactivity to CO₂ than IL in solution of high pH values, though there were four amino groups in IL molecular. As a result, sodium hydroxide showed priority to IL when competed to react with CO₂. In the light of this observation, relatively low absorbent concentration was favorable for more IL participating in CO₂ capture, while high absorbent concentration may not protrude the high absorption capacity of IL. On the other hand, the foam layers on semi-coke were relatively thin in a low concentration solution. Thus, the porous structure of semi-coke was favorable for CO₂ capture.

3.3 The effect of semi-coke on CO₂ absorption

The effect of semi-coke on CO₂ absorption was shown in Fig. 3(a). Compared to the absorption without filler, the CO₂ absorption mole ratio as controlling the outlet CO₂ concentration below 3 vol% increased from 0.53 to 0.92 when SN600 was used. The different CO₂ absorption capacities when SWT, S600N and SN600 were used revealed that the structure and surface properties of semi-coke were vital important for CO₂ capture. It is possible that the porous structure and functional groups resulted from nitric acid and heating treatment supplied more active sites for CO₂ absorption.
3.4 Absorption mechanism of NaOH/IL solution

Similar to aliphatic amines, in the absence of solvent, CO$_2$ could react with both primary and secondary amines on IL to form unstable carbamic acid: 

\[ 2\text{AmH} + \text{CO}_2 \rightleftharpoons \text{AmCO}_2^- + \text{AmH}_2^+ \]

\((\text{AmH is either primary or secondary amine})\)

It is indicated that two amino groups in the IL molecules interact with one CO$_2$ molecule.

With the presence of solvent, an alkyl carbonate is formed along with the protonated amine. As expressed: 

\[ \text{AmH} + \text{CO}_2 + \text{ROH} \rightleftharpoons \text{ROCO}_2^- + \text{AmH}_2^+ \]

the stoichiometric loading capacity is 1.

In this work, the CO$_2$ capture was taken place in NaOH/IL solution. Besides the reaction between NaOH and CO$_2$, it is noteworthy that water could participate in the absorption reaction. Additionally, water in solution could facilitate the secondary amines to be involved in CO$_2$ capture. The detail mechanism that accounting for the role of water in CO$_2$ capture by secondary amines was depicted in Fig.4(e).

IL-carbamate and protonated IL were formed by the nucleophilic attack of the amine lone pair to the CO$_2$ carbon. Subsequently, the nucleophilic reaction continued between the carbonyl atom of IL-carbamate and the oxygen of water, leading to the formation of bicarbonate. And then bicarbonate involved in the reaction with IL-amine to form IL carbamate and give back water. Additionally, when the concentration of NaOH was relatively high, there was a competing reaction for bicarbonate consuming: 

\[ \text{OH}^- + \text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}_2\text{O} \]

Therefore, much higher absorbent concentration would not exhibit higher CO$_2$ absorption capacity.

To confirmed the mechanism of the reactions and understand the characteristics of the reaction products,$^{13}$C NMR analysis was performed in Fig. 4(d). The resonance in the range of 159.89-163.91 ppm confirmed the emergence of IL-carbamate (C$_7$, C$_8$). The peaks of 159.89 ppm and 168.15 ppm were attributed to the existence of sodium bicarbonate and sodium carbonate, respectively.

3.5 The role of semi-coke in CO$_2$ capture

In order to figure out the absorption mechanism of semi-coke, the surface physical properties were examined. In Table 2, the specific surface area of SN600 was 11.435 m$^2$/g, which increased by 10.488 m$^2$/g. And the total pore volume was 0.01 cm$^3$/g, which increased by 0.009 cm$^3$/g. Combined with the
data of S600N, it is indicated that the modification method of combining nitric acid oxidation with heat treatment could effectively improve the specific surface area and porous structure. More micropores formed and the intrinsic pores were enlarged.

In modification process, nitric acid oxidation could dig pits and crevasses by penetrating into the surface. And the original pore structures of semi-coke would further be developed into larger pores. High temperature in the pyrolysis process could oxidize as well as release ash and organic volatiles jammed in the pores [8-9]. It seemed that semi-coke firstly treated with nitric acid was favorable for pore enlargement and surface area improvement, achieving a better absorption performance.

### Table 2 Surface physical properties of semi-coke samples

| Sample | S BET (m²/g) | Total pore volume (cm³/g) | Average pore size (nm) | Microporous volume (cm³/g) | Microporous average size (nm) |
|--------|--------------|--------------------------|-----------------------|---------------------------|-----------------------------|
| SWT    | 0.947        | 0.001                    | 2.214                 | 0.0004                    | 1.6859                      |
| S600N  | 7.224        | 0.006                    | 2.469                 | 0.0013                    | 1.6886                      |
| SN600  | 11.435       | 0.010                    | 2.558                 | 0.0010                    | 1.6668                      |

![Fig. 4 Characterization of absorbents and materials](image)

Raman spectra were used to analyze the structural changes of semi-coke samples. As is illustrated in Fig. 4(b), two bands located at 1595 and 1360 cm⁻¹ were detected in the spectra of S600N and SN600. The former one (1595 cm⁻¹) corresponds to the E₂g species of single-crystal graphite, while the latter one (1360 cm⁻¹) is assigned to be the vibration mode of the graphite lattice of which the Raman activity is originated from the loss of translational symmetry at the borders of the crystalline areas [10]. The shape changes at bands 1595 and 1360 cm⁻¹ revealed the structural differences resulted from the different degree of graphitization. This was consistent with XRD comparisons as showed in Fig. 4(a).
Fig. 4(c) shows the SEM images of the semi-coke samples S600N and SN600. It can be observed that the surfaces were dominated by pore-distributed structures. But the pore structures of the two types of semi-coke were quite different. For sample S600N, the folding on the surface was obvious, showing the layered structure in (I) and (II). Although concave and convex structures were observed, the cavities were relatively shallow. The interface between cavities was indistinct. It is indicated that the oxidation effects of nitric acid on graphitized carbon wall were not obvious. For sample SN600 in (III) and (IV), more obviously pore structure could be seen due to the formation of fragments when the sample was firstly treated with nitric acid for deashing. The fragments were mobile when heating, and were not tended to form graphitized structure [11]. The deep cavities created by the pieces of fragments were considered to increase the reactivity to CO₂. The detailed mechanism can be illustrated in Fig. 3(b).

4. Conclusion

The Poly-amino-based ionic liquid [TETAH][BF₄]/NaOH solution was used for CO₂ separation from biogas in a spray scrubber packed with modified semi-coke.

(1) A CO₂ mole ratio of 0.92 was achieved as controlling the outlet CO₂ concentration below 3% with the incorporation of modified semi-coke. A mole percentage of 20 % was favorable for improving CO₂ absorption capacity and absorption rate, capturing CO₂ into carbamate and bicarbonate.

(2) The porous structure of semi-coke could contribute to improving CO₂ absorption. Combining nitric acid oxidation with heat treatment, more micropores formed and the intrinsic pores were enlarged. Semi-coke firstly oxidized by nitric acid and then with heat treatment not only exhibited higher specific surface area and more porous structure, but also showed less degree of graphitization, which was suggested as possible to increase the reactivity to CO₂.

(3) Considering the easy synthesis of the ILs, the excellent absorption performance of ILs/NaOH solution as well as the easy availability of semi-coke, it is assumed that the absorption system in this research showed promising application in CO₂ separation from biogas as well as waste treatment.

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