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Capture of CO₂ from Natural Gas Using Ionic Liquids

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Abstract

This chapter will be divided into three parts; introduction, experimental and result and discussion.

Introduction: This includes introduction about ionic liquids, their history and types which were used in different applications such as removal of carbon dioxide from natural gas.

Experimental: This deals with chemicals, solvents, and scheme of synthesis of different types of ionic liquids and their characterizations using different traditional techniques. The synthesized ionic liquids were used to capture carbon dioxide from natural gas using bubbling technique and gas chromatography as indicator.

Result and discussion: The results which obtained from synthesis and the applications briefed in this section and the quality of removal will be determined.

Keywords: ionic liquids, bubbling technique, natural gas, carbon dioxide

1. Introduction

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Natural gas is the cleanest consuming non-renewable energy source, essentially because of its ignition creates low levels of carbon dioxide (CO_2) emissions; it is half the amount compared to coal and 30% compared to petroleum. Also it is widely available and easy to transport [1, 2].

For these reasons, there is a global trend for natural gas to be the main non-renewable energy source. According to the EIA (The Energy Information Administration), in 2011, the United States of America uses natural gas to produce 21% of its electricity and covering the equivalent of 24% of the energy demand. Global demand of natural gas, like the United States, is expected to increase or at least remains constant [3].

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Natural gas is divided into two types according to its source of extraction; the first type is conventional gas (relatively easy to recover) comes from relatively high permeable reservoirs such as siltstone, sandstone and carbonate reservoirs in which the rock pores act like a trap for the gas particles with permeability of more than 1000 microdarcy. On the other hand unconventional natural gas is found in low permeable reservoirs such as; coal bed, tight sand formations with permeability of 1–100 microdarcy and shale with permeability of 1 microdarcy or less, where the accumulation of gas have a tendency to diffuse and spread over extensive geological ranges making it more hard to extract [4].

2. General overview of shale gas

Shale gas is known as one of the unconventional natural gas; extracted from shale rocks and has risen as a standout among the most encouraging vitality sources in the last few decades. Shale revolution started in the United States of America, with the discovery of huge reserves of recoverable shale gas, and kept spreading out in other countries all over the world. [5, 6].

EIA [3] reported that; the shale gas production in the United States in 2005 was only about 2% from the produced natural gas. Nowadays, the U.S. has become the largest gas producer in the world, as shale gas represents about 34% of the total U.S. produced natural gas and it aims to be above 50% by the year 2040. It was reported that U.S. natural gas production will increase from 23 trillion cubic feet in 2011 to 33.1 trillion cubic feet in 2040, with an increase of 44%. Almost all of this increase in natural gas production is due to projected growth in the shale gas [3, 7]. There are many countries who once thought they were had no or limited amounts of conventional hydrocarbon reservoirs are finding and exploring shales for gas and oil. As shown in **Figure 1** beside USA, a lot of countries like Britain, Ukraine, south Africa, Canada, Brazil, Argentina, Mexico, Poland, Australia, china and several north African countries are interested in exploiting and development of shale gas industry [8].



Figure 1. Sedimentary basin worldwide containing significant shale gas resources. Source: U.S. Energy Information Administration [8].

3. Shale gas composition

Shale gas is a natural gas, mainly methane, was trapped within the shale rocks during the Devonian epoch. Shale rock like sandstone and limestone is a fine-grained sedimentary rock which formed by the accumulation of deposits at the surface of the earth or at the bottom of relatively closed bodies of water. Gases from conventional and unconventional reservoirs have relatively the same composition. Both contain various amounts of acid gases (H_2S and CO_2). Also the amount of produced water varies among formations. Shale gas is quite dry; on the contrary of coal bed methane production is accompanied with a lot of water [9].

4. Shale gas production

Although the sources of shale gas and its extraction techniques are known a long time ago, its extraction from very little resources has been considered economically only in the last few years. This is thanks to George Mitchell's ideas on hydraulic fracturing, horizontal drilling and well stimulation techniques [7].

5. Hydraulic fracturing

Hydraulic fracturing method is a well stimulating technique used to fracture the rocks of the reservoir. It consists of two main stages: the first one is injecting fracking fluid which is a high pressure fluid (fracking fluid consists mainly from water and suspended proppants such as sand or aluminum oxide with the aid of a thickening agent) into the reservoir to increase the downhole pressure and create cracks in the formation rocks. These cracks enable the trapped gases to flow. The second stage is known as flow-back in which some of the injected water is released and comes out to the surface with the produced gas. Flow-back fluids can be treated and reused in another hydraulic fracture job which can decrease the volume of the generated wastewater. After the fracking pressure effect is over, the sand grains or aluminum oxide holds the fractures open [8].

Recent advances in horizontal drilling and hydraulic fracturing techniques have allowed access to the production of large quantities of shale gas that were previously uneconomical to produce [4].

6. CO, removal

Removal of carbon dioxide increases the calorific value and transportability of the natural gas. Carbon dioxide content in the natural gas obtained from gas or oil well can vary from 4 to 50%. On the other hand, purged gas from a gas re-injected EOR (enhanced oil recovery) well can contain as much as 90% carbon dioxide. Before a natural gas rich in carbon dioxide can be transported, it must be pre-processed so as to meet the typical specification of 2–5%

carbon dioxide. To meet such a specification, the natural gas is most commonly treated with an aqueous alkanolamine solution in absorption columns. The major advantages of the amine treatment are that it is a widely commercialized technology in which the hydrocarbon loss is almost negligible. However, the capital and operating cost shoots up very rapidly as the concentration of carbon dioxide in feed gas increases [10].

Carbon dioxide, which falls into the category of acid gases (as does hydrogen sulfide, for example) is commonly found in natural gas streams at levels as high as 80%. In combination with water, it is highly corrosive and rapidly destroys pipelines and equipment unless it is partially removed or exotic and expensive construction materials are used. Carbon dioxide also reduces the heating value of a natural gas stream and wastes pipeline capacity. In LNG plants, CO₂ must be removed to prevent freezing in the low-temperature chillers.

7. Experimental

7.1. Materials

Lactic acid (99%), ethanol amine (99%), diethanolamine (99%) and N,N-dimethylethanolamine (99%) were purchased from Fluka. 1-Methyl imidazole (99%), 1,2 dimethylimidazole (98%), 2-bromoethylaminehydrobromide (98%), 3-bromopropylamine hydrobromide (99%), sodium tetrafluoroborate (99%) and lithium bis(trifluoromethylsulfonyl)imide (99%) were purchased from Sigma-Aldrich. Sodium methoxide (99%), ethanol (absolute), dry methanol (98%), acetone (99%), acetonitrile (99%) and methylene chloride (99%) were purchased from Merck Chemicals Company. PVDF membrane was obtained from Whatman incorporation.

7.1.1. Synthesis of ionic liquids (ILs)

7.1.1.1. Synthesis of ethanolamine lactates

Ethanolammonium ionic liquids were synthesized by direct neutralization of different ethanolamines with lactic acid [11].

Ethanolamines were loaded into 100 ml flask in water bath; the system was equipped with liquid filler, a reflux condenser and N_2 under vigorous stirring at constant rate. Lactic acid (0.05 mol) was then added drop wise into the stirring reaction mixture for about 15 min and the reaction was allowed to proceed for 30 min. The solution was treated with acetone, removed by evaporation under vacuum and then dried for 48 h at 50°C. The synthesized reaction for the ethanol ammonium ILs is expressed in **Scheme 1**:



Scheme 1. Synthesis of hydroxyl amine lactate. I: $(R = CH_{3'}R_1 = H, R_2 = H, R_3 = HO-CH_2-CH_2-)$; II, $(R = CH_{3'}R_1 = H, R_2 = HO-CH_2-CH_2-)$; II, $(R = CH_{3'}R_1 = H, R_2 = HO-CH_2-CH_2-)$; and III, $(R = CH_{3'}R_1 = CH_{3'}R_2 = CH_{3'}R_3 = HO-CH_2-CH_2-)$.

7.1.1.2. Synthesis of imidazolium bis(triflouromethylsulfonyl)imides

Solution containing one equivalent of 1-methyl imidazole (0.25 M) in acetonitrile was added to stirring solution of one equivalent n-bromoalkyl amine hydrobromide (ethyl and propyl, respectively), dissolved in a minimal amount of ethanol, it was stirred at room temperature. Solvent was removed under vacuum yielding dark solid color. Methylene chloride and ethanol (50:50)% were added to yield white precipitate and solvent was removed by evaporation. The amine moiety was deprotonated with 1.2 equivalence of sodium methoxide in dry methanol. Solvent was evaporated and methylene chloride was added to precipitate out the sodium bromide as by-product which was filtered off. Methylene chloride solution was added to 1.1 equivalence of lithium bis(tri fluoromethylsulfonyl)imide overnight and the organic layer was repeatedly washed with water to remove bromide. Methylene chloride ride and water were removed under vacuum. The synthesized product was expressed in **Scheme 2**.

7.1.1.3. Synthesis of imidazolium tetraflouroborates

Solution containing one equivalent of 1-methyl imidazole (0.25 M) in acetonitrile was added to a stirring solution of one equivalent of n-bromoalkyl amine hydrobromide (ethyl and propyl, respectively) dissolved in a minimal amount of ethanol, it was stirred at room temperature [12]. Solvent was removed under vacuum yields dark color. Methylene chloride was added to ethanol (50:50)% to yield white precipitate, and solvent was removed by evaporation. The amine moiety was deprotonated with 1.2 equivalence of sodium methoxide in dry methanol. Solvent was evaporated and methylene chloride was added to precipitate the sodium bromide as by-product which was filtered off. Methylene chloride solution was reacted with 1.1 equivalence of sodium tetraflouroborate, dissolved in water overnight and the organic layer was repeatedly washed with water. Methylene chloride and water were removed under vacuum. The synthesized reaction was expressed in **Scheme 3**.



Scheme 2. Synthesis of imidazolium bis(triflouromethylsulfonyl)imides. IV = (n = 2, $R_1 = CH_y R_2 = H$); V = (n = 3, $R_1 = CH_y R_2 = H$); VIII = (n = 2, $R_1 = CH_3 R_2 = CH_3$); and IX = (n = 3, $R_1 = CH_y R_2 = CH_3$).



Scheme 3. Synthesis of imidazolium tetraflouroborates. VI = (n = 2, $R_1 = CH_3$, $R_2 = H$); VII = (n = 3, $R_1 = CH_3$, $R_2 = H$); X = (n = 2, $R_1 = CH_3$, $R_2 = CH_3$); and XI = 3 (n = 3, $R_1 = CH_3$, $R_1 = CH_3$).

7.1.2. Capture of carbon dioxide (CO_2)

7.1.2.1. Bubbling technique

Using methanol as a blank solution, 0.1 mol solution of ionic liquid prepared, was put in the bubbling cell and the system run as follows [13, 14]:

- The system was adjusted as in **Figure 2** where: (a) cylinder of He, (b) cylinder of CO₂/CH₄, (c) valve, (d) water bath at 25°C, (e) bubbling cell, (f) needle, (g) mass flow meter, (h) sampling valve, and (i) gas chromatography.
- The system was evacuated using He gas first.
- CH_4/CO_2 gas were flowed to the system and passed to the solution through thin needle.
- Outlet gas was characterized by gas chromatography.



Figure 2. Flow sheet of CO₂ captures experimental apparatus.



Scheme 4. Mechanism for bubbling technique A (amine interaction).



Scheme 5. Mechanism for bubbling technique B, carbene interaction.



Scheme 6. Proposed amine interaction.

In amine interaction carbon dioxide is attacked by the amino group through it is lone pair of electrons, consequently the amino group of another molecule of ionic liquid capture a proton from the first one to form a bimolecular compound. In carbine reaction, the active proton of the imidazolium nucleus migrates to the amino group of the chain part to form the carbenium ion; this anion formed can attack the carbon dioxide molecule to get the Zwitterion (**Schemes 4** and **5**).

In this work the proposed mechanism is amine inter action and can be illustrated in **Scheme 6** [15].

7.1.2.2. Membrane technique (adsorption)

The system was adjusted as above (**Figure 2**), where bubbling cell was replaced by the membrane cell [(j) — membrane cell, (k) — supported ionic liquid membrane] (SILM) were prepared by immersing PVDF membrane in ionic liquid till saturation, put the SILM in membrane cell, pass CO₂/CH₄ through the cell, and the outlet gases passed to gas chromatography to be characterized.

7.1.3. Regeneration of ionic liquids

The used ionic liquids could be recycled by two ways. When we use heating, we can ride of captured CO_2 . Also by washing with distilled water and then evaporating it.

8. Results and discussions

8.1. Technique of CO₂ removal

Methanol was used as solvent for the prepared ionic liquid solutions as it has no effect on absorption of CO_2 ($CO_2 = 21.430$).

To reach the optimum conditions, the gas rate was changed and the percent of CO_2 captured was determined in presence of the prepared ionic liquid solutions. By using a rate of 0.7 sccm, the amount of ionic liquids took more time to be saturated with carbon dioxide, whereas by using a rate of 2 sccm we did not reach to a complete chemical reaction between the ionic liquids under investigation and the total amount of carbon dioxide flowed (**Figures 3** and **4**). While at 1 sccm rate, a complete reaction between the ionic liquid solutions and the flowed CO_2 took place with suitable time, i.e. the optimum rate was 1 sccm.

Figures 1–17 show that:

- The traditional ionic liquids (I–III) are of good efficiency in carbon dioxide removal from the natural gas and the order of increasing efficiency was II < III < I.
- The time of saturation of ionic liquids (I–III) by carbon dioxide followed the order of II < I < III.
- By using 1-methyl imidazole ionic liquids (IV–VII) in carbon dioxide capture, the results showed that the efficiency will be as follows: VII < VI < V < IV, this means that, the efficiency increased by:
 - a. Increasing the chain length of the aliphatic amine part.
 - **b.** Changing the anion part from bis(trifloromethylsulonyl)imide to tetraflouroborate so the second is better.
- This observation was also obtained by (VII–XI) ionic liquids.
- The derived imidazolium cations (1,2 dimethyl imidazole) affect the efficiency of synthesized ionic liquids as shown in the following order: XI < X < IX < VIII.

8.2. Regeneration of ionic liquids

Ionic liquids (I–XI) can be recycled. In chemical reaction the reacted species in the loaded solvent are decomposed by heating to liberate carbon dioxide and regenerate the ionic liquids that reacted with carbon dioxide. In another way, ionic liquids are recycled by washing them



Figure 3. Capture of CO₂ using ionic liquid vat rate 0.7 sccm.



Figure 4. Capture of CO₂ using ionic liquid VII at rate 2 sccm.



Figure 5. Conventional and non-conventional gas reservoirs [4].



Figure 6. Shale gas overall infrastructure block diagram [4].



Figure 7. Absorption of CO_2 using synthesized ionic liquid I.



Figure 8. Absorption of CO₂ using synthesized ionic liquid II.



Figure 9. Absorption of CO₂ using synthesized ionic liquid III.



Figure 10. Absorption of CO_2 using synthesized ionic liquid IV.



Figure 11. Absorption of CO₂ using synthesized ionic liquid V.



Figure 12. Absorption of CO_2 using synthesized ionic liquid VI.



Figure 13. Absorption of CO₂ using synthesized ionic liquid VII.



Figure 14. Absorption of CO₂ using synthesized ionic liquid VIII.



Figure 15. Absorption of CO₂ using synthesized ionic liquid IX.



Figure 16. Absorption of CO₂ using synthesized ionic liquid X.



Figure 17. Absorption of CO₂ using synthesized ionic liquid XI.



Scheme 7. Regenerated mechanism.



Figure 18. Absorption of CO_2 using regenerated ionic liquid I.



Figure 20. Absorption of CO₂ using regenerated ionic liquid III.



Figure 21. Absorption of CO₂ using regenerated ionic liquid IV.



Figure 22. Absorption of CO₂ using regenerated ionic liquid V.



Figure 23. Absorption of CO₂ using regenerated ionic liquid VII.



Figure 24. Absorption of CO₂ using regenerated ionic liquid X.

with distilled water, and consequently the captured carbon dioxide reacted with water to yield carbonate [16] (**Scheme 7**). Then, the ionic liquids were obtained by decantation and evaporation to get rid of any water. In this work, ionic liquids (VI, VIII, IX and XI) are soluble in water so, it cannot be regenerated through the second way. The regenerated ionic liquids are used to capture carbon dioxide from natural gas with high efficiency as shown in **Figures 18–24**.

Abbreviations

EIA	the Energy Information Administration
EOR	enhanced oil recovery
SILM	the supported ionic liquid membranes
sccm	standard cubic centimeters per minute

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