

# Development of a conceptual process for CO<sub>2</sub> capture from flue gases using ionic liquid

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## Abstract

The objective of this work is to develop a conceptual design of 1-butyl-3-methylimidazolium acetate ([bmim][Ac]) to capture 90 % of CO<sub>2</sub> from different scenarios. Each scenario includes flue gas dehydration, capture of at least 90 % of CO<sub>2</sub> from the feed, and compression to almost pure CO<sub>2</sub> for sequestration at 150 bar. In addition, the results showing the investment and operating costs are compared with those of the conventional MEA plant. The IL-based capture process is comparable with an MEA-based process at high CO<sub>2</sub> content.

**Keywords:** CO<sub>2</sub> capture, Ionic liquid, MEA, [bmim][Ac].

## 1. Introduction

The rapid growth of population, industry and agriculture is leading to the fast expansion of greenhouse gases (GHGs), which are often seen as a main factor of climate change. The global CO<sub>2</sub> emission had increased around 40 % from the year 1990 to 2008 (20.9 to 29.4 Gt). The largest emission of CO<sub>2</sub> results from electricity and heat generation with 41 percent of total CO<sub>2</sub> emission in 2010, followed by transportation (23 %), industry sector (10 %), and others (IEA 2013). It is predicted that 2986 - 7402 Gt of CO<sub>2</sub> is still discharged to the environment with continuous expansion of fossil-fuel based infrastructure until the end of this century (Davis et al. 2010). Therefore, a remarkable research effort has been allocated to development of modalities to lessen CO<sub>2</sub> emission and mitigate its adverse impact on the planet. CO<sub>2</sub> capture and storage (CCS) can play a key role in a reduction of industrial and stationary CO<sub>2</sub> emissions while allowing the continuous usage of fossil fuels such as coal, oil, and natural gas.

CO<sub>2</sub> is released from a variety of stack emissions and immediate chemical process streams. Flue gases from industrial processes normally have highly diverse compositions. It is noticeable that the CO<sub>2</sub> amount in flue gas streams can change from as low as 0.1 % to as high as 70 % or more. Typically, CO<sub>2</sub> content in flue gases from natural gas-fired power plants is in the range of 3 - 4 % while this factor in coal power stations equals 12 - 14 % CO<sub>2</sub>. In addition, about 7 % of CO<sub>2</sub> can be found in flue gas streams of typical refineries, 8 - 11 % in urea or natural gas processing, as well as 20 - 24 % in steel plants (Farla et al. 1995). Obviously, although CO<sub>2</sub> content changes in a wide range, there have been rarely researches on CO<sub>2</sub> capture in different industrial sources in contrast with those of power plants.

Several of the approaches that have been proposed to remove CO<sub>2</sub> from flue gases on a large scale include cryogenic distillation, purification with membranes, absorption with

liquids, and adsorption with solids (Aaron & Tsouris 2005). However, amines-based absorption processes are the most common separation technology while MEA is the most used solvent in many industries. An MEA-based systems can capture CO<sub>2</sub> at low partial pressure (7 - 16 mol %) along with stable operation, good reactivity, high absorption capacity, and low cost. On the other hand, the limitations of the MEA process are the corrosion because of high circulation rate and high loss and degradation of MEA. For these reasons, the normal concentration of MEA is usually limited to 30 wt. % or less. In addition, the principal thermodynamic limitation of MEA-based strippers are large amount of energy required to dissociate the chemical bonding between MEA and CO<sub>2</sub> (Fisher et al. 2007).

As a consequence, there is a need to explore other solvents that can have better performance in terms of specific regeneration energy and solvent circulation rate. Ionic liquids (IL) have been paid much attention owing to high CO<sub>2</sub> solubility, non-volatility, high thermal stability, and tunability of structure and properties. Studies on ILs for CO<sub>2</sub> capture have been promoted for several years in academia, government, and private companies. Also, several ILs-based conceptual processes are developed to compare against well-known conventional processes. Despite that, most studies on ILs are based on fixed feed gas compositions, and flow rates. Similarly, evaluation and comparison of economic performances are considered specific characteristics of the feed gas.

In this study, the ionic liquid 1-butyl-3-methylimidazolium acetate ([bmim][Ac]) was evaluated as chemical solvent by process simulation in Aspen Plus. The conceptual process for this IL is developed for different CO<sub>2</sub> contents. Subsequently, the capture costs of the cases are compared with conventional MEA based ones.

## 2. MEA-based scrubbing system

The MEA-based process is developed over a range of feed compositions (5 - 50 % CO<sub>2</sub>, 5.5 % H<sub>2</sub>O, 5.5 % O<sub>2</sub>, and the balance N<sub>2</sub>) at a flow rate of 360 kmol/h. The MEA-based capture unit is designed to meet the target of 90 % capture capacity with 90 % purity of CO<sub>2</sub> using 30 wt. % of MEA. A simplified flowsheet (absorber/stripper configuration) is represented in Figure 1. The ENRTL-RK thermodynamic package is used to describe the thermodynamics of dehydration and capture processes while the Peng-Robinson (PR) is employed for the compression section.

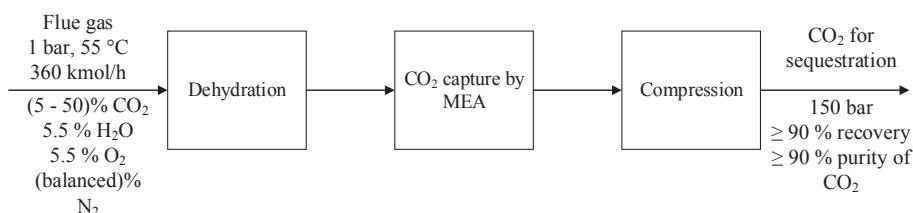


Figure 1 - Schematic diagram of the MEA-based system

The flue gas at high temperature is fed to the process using a blower at 1.5 bar. It then cooled to 35 °C using a direct contact cooler (DCC). This decreases the H<sub>2</sub>O composition of the feed from 5.5 to 4.4 % before entering to the absorber. The cool flue gas from the top of DCC is fed to the absorber at 35 °C while the lean MEA solvent flows to the top of the absorber. The number of stages for the absorber is 10 to achieve a rich amine loading of 0.45 mol CO<sub>2</sub>/mol MEA and 90 % recovery. In addition, the study

use the rate-based modelling approach and select the RADFRAC model. FLEXIPAC 250Y type metal packing is also used for all stages. The CO<sub>2</sub> concentration is reduced to less than 10 mol % at the exit of the absorber. A water wash is staged before CO<sub>2</sub> leaves the column to reduce MEA loss. The CO<sub>2</sub>-rich solution comes from the bottom of the absorber and is pumped through a rich/lean heat exchanger to the top of the stripping column with a temperature approach 5 K to exchange the duty with the hot stream that comes out from the reboiler. Before entered to the top of the stripper, the rich solvent is heated using a heater and flashed in a flash drum to recover some CO<sub>2</sub>. The stripper is a packed column with 10 stages. In the stripper, the rich solution flows countercurrent to the hot stream from the reboiler. CO<sub>2</sub> is recovered to the gas phase from the rich solvent. The lean solution is then cooled to 35 °C, and comes back to the top of the absorber. Some MEA and water are lost by the gas streams from the columns; to make-up for this MEA and water are supported with the lean solvent.

The CO<sub>2</sub> discharged from the stripper are condensed and remove a significant amount of water by a partial condenser and flash drum. The gaseous CO<sub>2</sub> is then sent to a multistage compressor chain with four stages. Finally, the compressed CO<sub>2</sub> is discharged at 150 bar by a pump for sequestration.

### 3. IL-based scrubbing system

ILs are a class of low temperature molten salts, which are composed of an organic cation and an inorganic anion (Liu et al. 2016). In this study, the selection of 1-butyl-3-methylimidazolium acetate ([bmim][Ac]) was chosen because of its chemical absorption behaviour as described by Shiflett (Shiflett et al. 2010). The simplified flow diagram for the IL process is shown in Figure 2. The modified NRTL-RK thermodynamic package is used to describe the thermodynamics of dehydration and capture processes while the Peng-Robinson (PR) is employed for the compression section. The inlet flue gas concentration was the same as the MEA base cases.

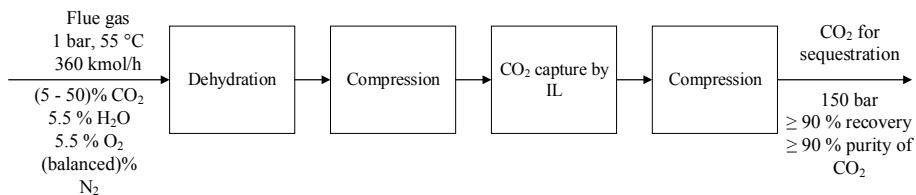


Figure 2 - Schematic diagram of the IL-based system

Similar to the MEA-based process, the hot flue gas is compressed to 1.5 bar before cooled to 35 °C at the DCC. The cool flue gas from the top of DCC is then compressed again to 7.9 bar before entering the absorber. The absorption column is simulated using RADFRAC along with FLEXIPAC 250Y type metal packing for all 10 stages. The solvent is cooled to 25 °C before it is fed to the top of the absorber. The clean gas is vented from the top of the column. Because of a very low vapour pressure of IL, a water-wash section is not necessary. The regeneration of IL is completely different from the conventional process. In this case, the IL is recovered by a reduction of pressure and high temperature. The lean solvent coming from the bottom of the flash tank is pumped back through a heat exchanger and cooler before recycling to the top of the absorption

column. Due to a very low vapour pressure of IL, there is only CO<sub>2</sub> in the vapour phase of the flash tank. Also, assuming there is no make-up IL stream supported with the lean solvent. Finally, the gaseous CO<sub>2</sub> is sent to the multistage compressor chain with five stages, and discharged at 150 bar by a pump for sequestration.

#### 4. Results and Discussion

Table 1 to 3 provide more details for the MEA and IL-based processes in three scenarios in which variable molar composition of CO<sub>2</sub> from as low as 5 % mol to as high as 50 % mol. All processes using MEA and IL solvents have the possibility to separate more than 90 % of CO<sub>2</sub> as well as purity of above 90 % from flue gas slip streams. It is important to notice that IL-based processes are able to achieve a higher recovery of above 97 % compared to the conventional ones. However, the purity of those processes are just little lower than those values from MEA-based systems.

As can be seen from Table 1 to 3, the mass flowrates of ILs required to capture 90 % mol of CO<sub>2</sub> from flue gases are always higher than those of MEA in all scenarios. The higher mass flowrate of IL is a result of a lower CO<sub>2</sub> solubility. It is noted that increasing absorption pressure and decreasing temperature can improve physical absorption. Similarly, desorption of CO<sub>2</sub> from IL requires a low pressure and high temperature to achieve the desired target of recovery and purity of CO<sub>2</sub>. However, there are always trade-offs in selecting pressure and temperature for each equipment, which might affect the next steps.

Table 1 - Operating conditions for MEA and IL at 5 % mol of CO<sub>2</sub>

	MEA			IL		
	T (°C)	P (bar)	m (kg/h)	T (°C)	P (bar)	m (kg/h)
Absorber						
Flue gas	35.1	1.4	10,158.04	35	7.71	9,946.43
Vent gas	48.6	1.01	9,922.03	25.4	6.18	9,166.25
Absorbent inlet	35	1.4	11,203.57	25	7.91	36,940.38
Absorbent outlet	37.8	1.01	11,942.32	38.36	6.19	37,720.56
Stripper/Flash						
CO <sub>2</sub> outlet	106.9	1.7	1,464.14	127	0.25	780.15
Absorbent inlet	108.7	2.06	11,807.13	135	4.19	37,720.56
Absorbent outlet	118	1.7	11,203.48	127	0.25	36,940.4

Table 2 - Operating conditions for MEA and IL at 20 % mol of CO<sub>2</sub>

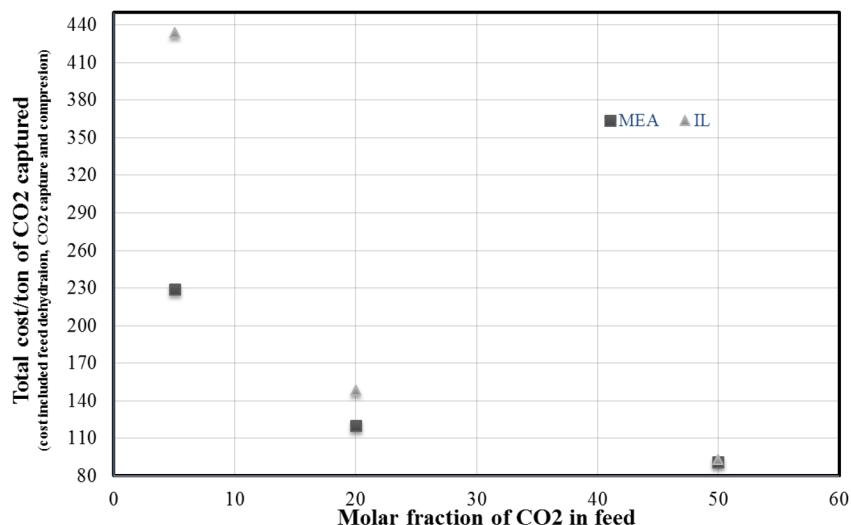
	MEA			IL		
	T (°C)	P (bar)	m (kg/h)	T (°C)	P (bar)	m (kg/h)
Absorber						
Flue gas	34.9	1.4	11,018.6	35	7.708	10,809.97
Vent gas	60.5	1.01	9,109.6	25.82	6.18	7,667.89
Absorbent inlet	35	1.4	44,566.21	25	7.91	83,631.37
Absorbent outlet	55	1.02	47,508.32	44.82	6.19	86,773.45
Stripper/Flash						
CO <sub>2</sub> outlet	107.6	1.7	6,019.08	121.78	0.25	3,142.1
Absorbent inlet	108.6	2.06	46,933.22	135	4.19	86,773.45
Absorbent outlet	118	1.70	44,564.81	121.78	0.25	83,631.32

Table 3 - Operating conditions for MEA and IL at 50 % mol of CO<sub>2</sub>

	MEA			IL		
	T (°C)	P (bar)	m (kg/h)	T (°C)	P (bar)	m (kg/h)
<b>Absorber</b>						
Flue gas	34.8	1.4	12,745.9	35	7.71	12,536.96
Vent gas	74.5	1.01	7,164.48	25.82	6.18	4,621.63
Absorbent inlet	35	1.4	99,114.71	25	7.91	167,352
Absorbent outlet	63.2	1.02	106,461.43	48.6	6.19	175,267
<b>Stripper/Flash</b>						
CO <sub>2</sub> outlet	107.4	1.7	13,304.87	118.73	0.25	7,915.21
Absorbent inlet	108.3	2.06	103,995.7	135	4.19	175,267
Absorbent outlet	118	1.7	99,113.41	118.73	0.25	167,352

To compare both processes an economic evaluation is executed using the Aspen Process Economic Analyser (APEA) to estimate the equipment costs as well as operating costs. The CO<sub>2</sub> captured costs against molar fraction of CO<sub>2</sub> in feed are plotted for all scenarios in Figure 3.

As presented in Figure 3, the total cost for CO<sub>2</sub> capture using MEA changes from 230 \$/t of CO<sub>2</sub> to 90 \$/t when the molar composition of CO<sub>2</sub> is from 5 to 50 %, respectively. Those values are in agreement with other estimates (151 \$/t of CO<sub>2</sub> at 14 % volume of CO<sub>2</sub> (Schach et al. 2010)). In the meanwhile, the cost of capturing CO<sub>2</sub> by using IL at 5 % are twice as much as that of the MEA-based system, (more 400 \$/t). This values gradually reduces to 150 \$/t and 92 \$/t when CO<sub>2</sub> content is at 20 % and 50 %, correspondingly. Obviously, only at high CO<sub>2</sub> concentration the IL-based systems is economically competitive with conventional process. Currently, the cost of buying MEA is about 1.31 \$/kg while of that for IL is 20 \$/kg, more than 10 times higher; this explains the differences. It is further noticeable that all cases only capture 3 - 4 % of the total CO<sub>2</sub> emissions. As a consequence, when 90 % of the total CO<sub>2</sub> emissions is captured at large-scale plants, the calculated costs will become more realistic.

Figure 3 - Total costs for the MEA- and IL-based CO<sub>2</sub> processes in different scenarios

## 5. Outlook and Conclusions

The outcomes of this study show good performance with 90 % of CO<sub>2</sub> capture at high purity (> 95 %). The result shows that the costs related to both solvents are high at all CO<sub>2</sub> concentration; however, all cases are captured at small-scale (3 - 4 % of total CO<sub>2</sub> emissions). Modelling indicates that the CO<sub>2</sub> captured cost of IL process is always higher than that of MEA-based process, two times higher at low CO<sub>2</sub> content and nearly same at high CO<sub>2</sub> content. However, the cost of buying IL is nearly 15 times higher than that of MEA. Obviously, if the cost of IL decreases to 10 \$/kg because of production of multi-ton quantities, the cost of capturing CO<sub>2</sub> by IL will be equal to that of MEA at low CO<sub>2</sub> content and lower at higher CO<sub>2</sub> content. In addition, degradation of MEA at high temperature was not evaluated in this study. Compared to MEA, IL is quite stable at operating conditions, which allows reducing operating costs of IL in a long term. Corrosion is also another problem of MEA when high circulation rate is used. ILs with adjusted structures show negligible corrosion to most of normal construction materials in the chemical industry. As a result, IL-based systems will become potential candidates that can be used for separating CO<sub>2</sub> from different emission sources.

Next the modelling of IL-based systems with higher flue gas flowrates will be conducted. In addition, a new solvent mixing IL and MEA which could take advantages of both solvents will be developed for a more cost-effective and better-performing system.

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