



This is a repository copy of *Process analysis and economic evaluation of mixed aqueous ionic liquid and monoethanolamine (MEA) solvent for CO₂ capture from a coke oven plant.*

White Rose Research Online URL for this paper:
<http://eprints.whiterose.ac.uk/133000/>

Version: Accepted Version

Article:

Oko, E. orcid.org/0000-0001-9221-680X, Zacchello, B., Wang, M. orcid.org/0000-0001-9752-270X et al. (1 more author) (2018) Process analysis and economic evaluation of mixed aqueous ionic liquid and monoethanolamine (MEA) solvent for CO₂ capture from a coke oven plant. *Greenhouse Gases: Science and Technology*, 8 (4). pp. 686-700. ISSN 2152-3878

<https://doi.org/10.1002/ghg.1772>

This is the peer reviewed version of the following article: Oko, E. , Zacchello, B. , Wang, M. and Fethi, A. (2018), Process analysis and economic evaluation of mixed aqueous ionic liquid and monoethanolamine (MEA) solvent for CO₂ capture from a coke oven plant. *Greenhouse Gas Sci Technol.*, which has been published in final form at <https://doi.org/10.1002/ghg.1772>. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Self-Archiving.

Reuse

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk
<https://eprints.whiterose.ac.uk/>

Process analysis and economic evaluation of mixed aqueous ionic liquid and monoethanolamine (MEA) solvent for CO₂ capture from a coke oven plant

Eni Oko¹, Baptiste Zacchello², Meihong Wang^{1,*}, Aloui Fethi²

¹Department of Chemical and Biological Engineering, The University of Sheffield, S1 3JD, UK

²Department of Mechanical and Energetics, School of Engineering, ENSIAME, Valenciennes 59313, France

*Corresponding Author: Tel.: +44 11142227160. E-mail address: Meihong.Wang@sheffield.ac.uk

Abstract

This study investigates the process and economic impacts of using an aqueous mixture of 1-butylpyridinium tetrafluoroborate ([Bpy][BF₄]) ionic liquid (IL) and monoethanolamine (MEA) as the solvent for CO₂ capture from a coke oven plant. The gaps highlighted in the literature on the study of an aqueous mixture of IL and MEA for CO₂ capture include lack of detailed process models and information on the impacts of varying the IL concentration on different process conditions and economics. This study addressed these needs by developing a rate-based solvent-based CO₂ capture process model with mixed IL and MEA solvent and using the model to perform process and economic evaluation. The model was developed with Aspen Plus® and was used to investigate seven different aqueous mixtures of IL and MEA. The MEA concentration was 30 wt% for all the seven aqueous solvent mixtures, and the corresponding IL concentration was 0, 5, 10, 15, 20, 25 & 30 wt% for each combination. The hybrid IL solvent mixtures (i.e. 5-30 wt% IL) have 7-9% and 12-27% less regeneration energy and solvent circulation rate respectively compared to the base case (i.e. 30 wt% MEA). Based on a commercial-scale cost benchmark for the IL, the initial solvent cost for the mixed solution is predictably higher. However, the solvent makeup cost is less for the mixed solvent.

Keywords: Carbon Capture; Monoethanolamine (MEA); Ionic liquid; Process simulation, Economic analysis, Industrial carbon capture

Nomenclature

$A, B, C \text{ \& } D$	Parameters for equilibrium constant equation
A_i, B_i, C_i	Parameters for vapour pressure equation (Eqn 1)

$C_{1i}-C_{3i}$	Parameters for vapour pressure equation (Eqn 1)
$C'_{1i}-C'_{3i}$	Parameters for heat capacity equation (Eqn 2)
$C''_{1i}-C''_{5i}$	Parameters for surface tension equation (Eqn 5)
$C'''_{1i}-C'''_{3i}$	Parameters for thermal conductivity equation (Eqn 6)
C_i	Component molar concentration (mol/L)
C_{pi}	Heat capacity (J/kmol K)
E	Activation energy (J/kmol)
k	Pre-exponential factor
K_{eq}	Equilibrium constant
M_i	Molar mass (kg/kmol)
P_{ci}	Critical pressure (Pa)
P_i	Vapour pressure (Pa)
r	Reaction rate (mol/m ³ s)
R	Ideal gas constant (J/mol K)
T	Temperature (K)
T_r	Reduced temperature
T_{ci}	Critical temperature (K)
$Z_i^{*,RA}, d_i$	Parameters for density equation (Eqn 3)

Greek Letters

σ_i	Surface tension (N/m)
λ_i	Thermal conductivity (W/m K)
η_i	Liquid dynamic viscosity (Pa s)
ρ_i	Liquid density (kg/m ³)

1 Introduction

1.1 Background and motivation

Carbon capture and storage (CCS) technology is the most sustainable and economical option for decarbonizing large stationary CO₂ emitters such as power plants and carbon-intensive industries ¹ such as iron steel plant, cement plant, and refineries. The technology involves capturing CO₂ from these sources and transporting them to underground storage sites such as saline aquifer and depleted oil and gas reserves, where they are either stored permanently or used for enhanced oil recovery (EOR) purposes. ¹ Currently, solvent-based carbon capture through chemical absorption is the only commercially available technology for deploying CCS.

² In this process, 30 wt% MEA solution is commonly used as the solvent for capturing CO₂. ³

However, the solvent has unacceptable characteristics including high regeneration energy of about 4.2 GJ/ton CO₂,⁴ high solvent circulation rate leading to large equipment sizes,⁵ poor recyclabilities with the solvent make-up cost of approximately US\$0.19-1.31/ton CO₂,⁶ high thermal and chemical degradability,⁷ high corrosivity⁸ and environmentally unfriendly.⁹

To address these problems, solvents with better attributes regarding regeneration energy requirement, circulation rate, recyclability, chemical and thermal stability and environmental benignity should replace the commonly used 30 wt% MEA solvent in this process. Ionic liquids (ILs) have shown great promise in this regard although they have slower kinetics and are more expensive than aqueous MEA solvent.¹⁰⁻¹³ However, mixed IL and MEA solvent could leverage on the positive attributes of both solvents resulting in a better and cost-effective option.

14

1.2 Literature review

ILs are organic salts with poorly coordinated ions which results in them being liquid below 100°C, or even at room temperature.⁹ ILs are derived from a combination of different cations (e.g., imidazolium, pyrrolidinium, pyridinium) and anions (e.g., hexafluorophosphate, chloride, and tetrafluoroborate). There are mainly two classes of ILs – room temperature ionic liquids (RTILs) and task-specific ionic liquids (TSILs) – and their detailed review is well reported in literature^{6,10,13} including comparison with molecular organic solvents such as amines.¹⁵ The study in this section discusses the application of different IL-based solvents in solvent-based carbon capture processes.

1.2.1 Room temperature ionic liquids (RTILs)

RTILs are unfunctionalised ILs.⁶ CO₂ absorption in RTILs is mainly through physical absorption.¹⁰ The enthalpy change of CO₂ physical absorption by RTILs is generally about 20 kJ/mol which results in lower regeneration energy requirement than for amine solutions.¹⁰ However, CO₂ solubility in RTILs at near atmospheric conditions which is typical in solvent-based capture

processes is minimal, about 5 mol%, even for the best RTILs. ⁶ Appreciable CO₂ solubility is only possible at higher pressure (up to 60 bar). Anion fluorination and increasing the cation alkyl side chain have been shown to improve CO₂ solubility. ^{6,10} RTILs also have a very high viscosity, up to 100 mPa.s at 25°C in contrast to 30 wt% MEA solution which has about 2.50 mPa.s viscosity at 25°C. As a result, they are unsuitable for use in solvent-based capture process at near atmospheric condition. These poor characteristics can be enhanced by mixing RTILs with other solvents (see Section 1.2.3).

1.2.2 Task-specific ionic liquids (TSILs)

TSILs are functionalized and potentially absorb CO₂ through chemical and physical absorption. ^{6,10} At low pressure (below 2 bars), absorption is mainly through a chemical reaction in the same way as in aqueous alkanolamines. As pressure increases, physical absorption gradually dominates. TSILs can absorb 1 mol of CO₂ per 2 mol of the solvent by a rapid and reversible mechanism as in alkanolamines, and the reaction can be reversed by heating the loaded solution between 80-100°C.

Shiflett et al. ¹⁶ developed an equilibrium-based PCC model using 1-Butyl-3-methylimidazolium Acetate ([BMIM][Ac]) TSIL as solvent. The performance of the solvent was compared with reference 30 wt% MEA solvent. Their results showed that the IL-based process could reduce the reboiler duty by about 16% compared to MEA solvent. They also showed that the capital cost and equipment footprint for the process with IL solvent are respectively 11% and 12% lower than with 30 wt% MEA solvent.

Due to the high cost of TSILs, up to US\$40/kg (futuristic large-scale production estimate by BASF) compared to about US\$1.25/kg for MEA, it is predicted that solvent cost for this process will be high. However, significant savings could be made due to the reduced solvent makeup. ⁶ Also, they have slow reaction kinetics with CO₂. Their slow reaction kinetics will increase residence time requirement for the solvent-based capture process and further hinder their ability

to cope with rapid load changes in the upstream plant. Finally, their viscosity is high and as a result resistance to mass transfer is significant. These factors diminish their prospects in the treatment of industrial flue gases.

1.2.3 Hybrid IL solvents

Hybrid IL solvents, obtained by mixing IL with other solvents such as water and alkanolamines, is a response to the drawbacks of IL highlighted in Sections 1.2.1 and 1.2.2. Wappel et al.¹⁷ showed that a mixture of ILs and water performs better than using only IL but still slower reaction kinetics and lower absorption capacity than 30 wt% MEA solution.¹⁷ Other studies show that mixed ILs and alkanolamines have better absorption and stripping performance^{14,18-19} than both ILs only and 30 wt% MEA solution. Studies by Yang et al.¹⁹ also showed that MEA losses for mixed IL and MEA solvent are lower than 30 wt% MEA solvent.¹⁹ Huang et al.¹² presented an equilibrium-based solvent-based capture model for different aqueous hybrid IL solvents namely [Bmim][BF₄]-MEA, 1-butyl-3-methylimidazolium dicyanamide ([Bmim][DCA])-MEA, 1-butylpyridinium tetrafluoroborate ([Bpy][BF₄)]-MEA.¹² Their results showed that [Bpy][BF₄]-MEA solvent reduces the heat duty and the capture cost by 15% and 11% respectively compared to reference MEA solvent (i.e., 30 wt% MEA solution). Zacchello et al.²⁰ presented a rate-based solvent-based capture model for [Bpy][BF₄]-MEA hybrid solvent.²⁰ The model was used to investigate the impact of IL fraction in the mixed solvent on solvent circulation rate and reboiler duty for CO₂ capture from a coke oven plant. In conclusion, mixed ILs and alkanolamines have better all-around attribute than either IL only or 30 wt% MEA solvent. Rate-based solvent-based capture model for mixed solvent has been developed in Zacchello et al.²⁰ and used to investigate the impact of IL fraction in mixed IL and MEA solvent on solvent circulation rate and reboiler duty. The effect of IL fraction on other critical operating variables and operating cost to substantiate conclusions in Zacchello et al.²⁰ is yet to be reported.

1.3 Aim of this study and Novelty

The literature summarised in Section 1.2 suggests that IL only are unsuitable for flue gas treatment at near atmospheric conditions due to their high viscosity, low CO₂ solubility and slow reaction kinetics with CO₂. Adding solvents such as MEA to ILs could improve their absorption performance by lowering their IL viscosity and enhancing their reaction kinetics and absorption capacity. The performance of mixed IL and other solvents have been demonstrated with process models of solvent-based carbon capture^{12,16,20} and through experimental investigations.^{14,17-19} However, there are no evaluations of the impacts of different IL fraction in the hybrid solvent on the vital process and economic variables such as temperature profile in absorber and stripper, solvent make-up cost, steam and pumping duty. Such analysis will be a useful guide for determining optimal IL fraction for the mixed solvent. Many published studies suggested over 30 wt% IL fraction for the combined solution but the preliminary research by Zacchello et al.²⁰ suggests this may be somewhat too high as based on predicted prices (industrial scale) of common IL solvents, the solvent cost could become very significant.

This study aims to address these needs through simulation of the process for mixed [Bpy][BF₄] IL and MEA solvent using rate-based model. Most models for hybrid IL solvent are equilibrium-based models^{12,16} and previous studies²¹⁻²² show that they are not very accurate. Zacchello et al.²⁰ has introduced rate-based model for hybrid IL solvent but have relied on default property parameters in Aspen Plus[®].²⁰ The novelties in this study are summarized as follows:

- Improved rate-based model for the process. Default parameters namely eNRTL binary interaction parameters among others have been used in Zacchello et al.²⁰ In this study, the parameters have been replaced by new values obtained through regression of experimental data.²³⁻²⁵ The model in this study is therefore potentially more accurate than the one presented in Zacchello et al.²⁰

- Additional process analysis using the improved rate-based model involving evaluation of the impact of IL fraction on temperature profile, L/G ratio, and regeneration energy is included in this study.
- Finally, economic analysis using the improved rate-based model was carried out. The economic analysis involves evaluation of the impact of the IL fraction on solvent make-up cost, costs of steam and pumping duty. The argument of Zacchello et al.²⁰ that the initial solvent cost for mixtures with IL fractions greater than 5 wt% may not be economically competitive is valid. However, the findings of this study show that savings in solvent makeup cost is substantial and in long-term could offset the initial solvent cost for higher IL concentration.

2 Description of solvent-based capture process

The solvent-based capture process (Fig.1) comprise of CO₂ absorber and stripper and other ancillary unit operations, namely heat exchangers, pumps, mixing tanks, etc. Flue gas from an industrial process (or fossil fuel-fired power plant) is cooled to about 40°C before entering the absorber. In the absorber, CO₂ in the flue gas is removed mainly by chemical reactions with a counter-current stream of solvent to form a weakly bonded compound.²⁶ The treated gas is then water washed (to recover entrained solvents) before they are released into the atmosphere.

Before entering the stripper, the CO₂ rich solvent from the absorber is heated to about 100°C in a cross heat exchanger by regenerated (or lean) solvent from the stripper. In the stripper, the rich solvent is further heated it to about 120°C at a pressure of approximately 1.8 bar. The condition reverses the chemical reaction resulting in the release of the captured CO₂. The stripper overhead stream (up to 99 wt% CO₂) is then compressed and transported through a pipeline to sequestration sites while the lean solvent from the stripper bottom is pumped back to the absorber.

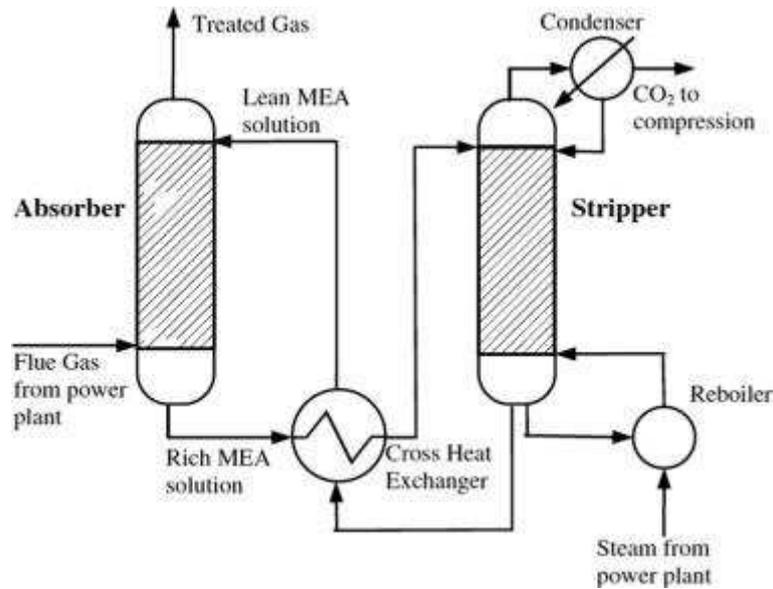


Fig. 1 Schematic diagram of solvent-based capture process ¹

3 Model development

3.1 Benchmark for model comparison

At the moment, there are no published experimental data of solvent-based capture process with mixed IL and MEA solvent. As a result, a published model of the process ¹² is used as a benchmark for this study. The model ¹² has been selected as the thermodynamic and transport properties of the selected IL and process conditions are available, making it possible for the model to be duplicated. The model in Huang et al. ¹² was simulated in Aspen Plus[®] using RADFRAC equilibrium stage model. ¹²

Table 1 Input conditions ¹²

	Flue Gas	Lean Solvent
Temperature (°C)	35	40
Mole Flow (kmol/hr)	20114.09	28762.98
Mass Flow (kg/hr)	580960	1103880
Pressure (bar)	1.1	1.0
Mass Frac (wt %)		
MEA	0	30
C ₉ H ₁₄ ⁻¹	0	30

H ₂ O	13.62	40
CO ₂	10.34	0
N ₂	71.73	0
O ₂	4.32	0

The flue gas specification (Table 1) is based on the outlet of coke oven combustion chambers at Shanxi Coke Plant in China.¹² Coke production is an integral part of the iron and steel making industry, and direct CO₂ emissions from the coke oven are about 18% of total emissions from the industry.²⁷ The flue gas is assumed to have been desulphurized, and the CO₂ concentration is 10.34 wt%, slightly higher than CO₂ in the natural gas power plant flue gas. The selected IL is [Bpy][BF₄], a pyridinium-based IL with good solubility properties in MEA. The [Bpy][BF₄] IL has excellent potential for large-scale applications than the more famous imidazolium-based IL due to their lower cost, toxicity, and environmental benignity.²⁸⁻³⁰ The input conditions given in Tables 1 and 2 were used to develop the model.

Table 2 Other conditions¹²

Items	Unit	Value
Absorber		
Pressure of the column bottom	bar	1.1
Pressure drop	Bar	0.1
Gas inlet temperature	°C	35
Liquid inlet temperature	°C	40
Stage number		14
Murphree efficiency	%	25
Stripper		
Pressure of the column bottom	bar	1.8
Pressure drop	bar	0.1
Stage number		14
Molar reflux ratio		0.5
Murphree efficiency	%	25
Rich solvent pump		
Outlet pressure	bar	2
Efficiency	%	75

3.2 Thermo-physical properties

The phase equilibrium, chemical equilibrium and reaction enthalpy of the CO₂ absorption/stripping system were modelled using Electrolyte Non-Random-Two-Liquid (eNRTL) thermodynamic model available in Aspen Plus[®]. The thermodynamic model has been commonly adopted in modelling MEA scrubbing processes in existing publications.^{5,22,31} In contrast, to Zacchello et al.,²⁰ the default binary interaction parameters for CO₂-H₂O-MEA and electrolytes pair among others in Aspen Plus[®] have been updated with more reliable data from published studies (Table 3). The CO₂-[Bpy][BF₄], H₂O-[Bpy][BF₄] and MEA-[Bpy][BF₄] interaction parameters and Henry constant parameter for CO₂-[Bpy][BF₄] were obtained from Huang et al.¹². Physical properties of the MEA-H₂O-CO₂-IL system are based on Aspen Plus Database³² and published data.^{12,25,33}

Table 3 Updated model parameters

Parameters	Source
NRTL binary	Yan and Chen ²⁴ and Zhang et al. ²⁵
Electrolyte pair	Zhang et al. ²⁵
Henry constant	
CO ₂ -H ₂ O	Yan and Chen ²⁴
CO ₂ -MEA	Liu et al. ²³

The temperature dependent properties, namely heat capacity, density, vapour pressure, viscosity, surface tension and thermal conductivity were obtained using the equations below available in Aspen Plus[®] database. The equation parameters for the IL have been obtained Huang et al.¹²

Vapour pressure

$$\ln P_i = C_{1i} + \frac{C_{2i}}{T + C_{3i}} \quad (1)$$

Heat capacity

$$C_{pi} = C'_{1i} + C'_{2i}T + C'_{3i}T^2 \quad (2)$$

Density

$$\rho_i = \frac{M_i P_{ci}}{RT_{ci} [Z_i^{*,RA} (1 + d_i (1 - T_r))]^{[1+(1-T_r)^{2/7}]}} \quad (3)$$

Viscosity

$$\ln \eta_i = A_i + \frac{B_i}{T} + C_i \ln T \quad (4)$$

Surface tension

$$\sigma_i = C_{1i}'' \left(1 - \frac{T}{T_{ci}}\right)^{(C_{2i}'' + C_{3i}'' T_{ri} + C_{4i}'' T_{ri}^2 + C_{5i}'' T_{ri}^3)} \quad (5)$$

Thermal conductivity

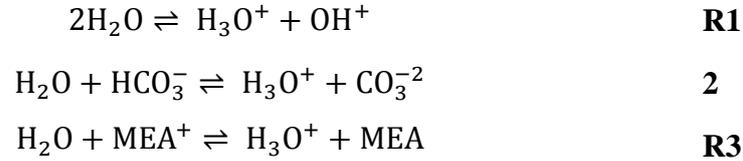
$$\lambda_i = C_{1i}''' + C_{2i}''' T + C_{3i}''' T^2 \quad (6)$$

3.3 Reaction chemistry

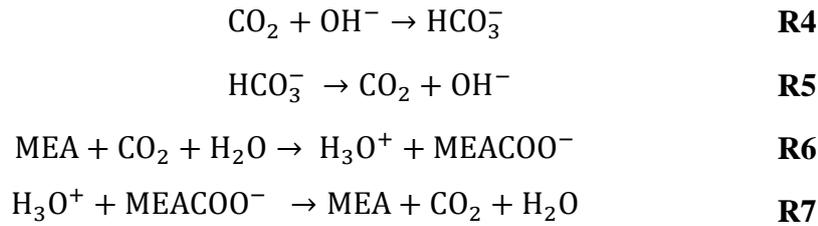
Only MEA undergo reactions with CO₂, the IL absorb CO₂ through physical absorption only.

The reaction chemistry involving H₂O-CO₂-MEA is comprised of both equilibrium and rate-controlled reactions.³⁴

The equilibrium reactions are defined as:



On the other hand, the rate-controlled reactions are defined as:



The equilibrium constant for **R1-R3** is estimated as follows:

$$\ln(K_{eq}) = A + \frac{B}{T} + C \cdot \ln(T) + D \cdot T \quad (7)$$

On the other hand, the reaction rate for the rate-controlled reactions **R4-R7** is determined

using the power law expression as follows:

$$r = k \exp\left(-\frac{E}{RT}\right) \prod_{i=1}^N C_i \quad (8)$$

The parameters for the equilibrium constant and power-law expression are given in Table 4.

Table 4 Parameters for Eqn 7 & 8 ³⁴

Reactions	A	B	C	D
R1	132.889	-13445.9	-22.4773	0
R2	216.05	-12431.7	-35.4819	0
R3	-3.03833	-7008.36	0	-0.0031349

	K	E (J/Kmol)
R4	4.32E+13	5.55E+07
R5	2.38E+17	1.23E+08
R6	9.77E+10	4.13E+07
R7	3.23E+19	6.55E+07

3.4 Model comparison

The model in Huang et al. ¹² duplicated in this study cannot be validated because there is no process or experimental data for the mixed IL and MEA solvent. It has instead been compared to the original model in Huang et al. ¹² to demonstrate the consistency of the model. The topology of the duplicated model in Aspen Plus[®] is shown in Fig.2. The comparison results of the replicated model and the benchmark model ¹² are shown in Tables 5 and 6. The results showed good agreement indicating accurate representation of the Huang et al. ¹² model.

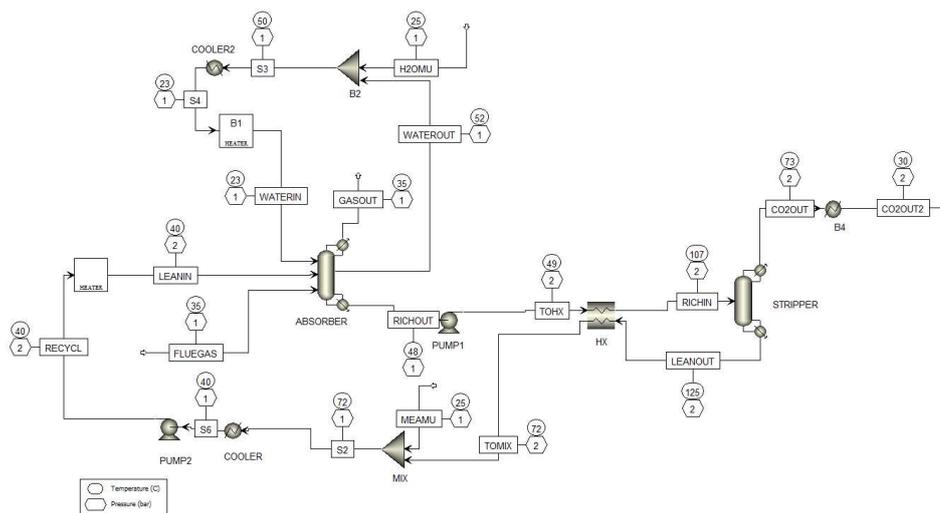


Fig. 2 Model topology of the process in Aspen Plus[®]

Table 5 Stream results for Absorber

Variables	FLUEGAS (Sour gas)			LEANIN			RICHOUT			GASOUT (Sweet gas)		
	This Work	Huang et al. ¹²	Rel. Error (%)	This Work	Huang et al. ¹²	Rel. Error (%)	This Work	Huang et al. ¹²	Rel. Error (%)	This Work	Huang et al. ¹²	Rel. Error (%)
Temp. (°C)	35	35	0.000	40	40	0.00	49.5	50	1.000	34.3	35	2.000
Mass Flow (kg/hr)	580960	580960	0.000	1079245	1103880	2.232	1127496	1132710	0.460	532435	520730	2.248
Loading (mol CO ₂ /mol MEA)				0.205	0.20	2.500	0.542	0.550	1.455			
CO₂ flow (kg/hr)	67130	67130	0.000							6580	6490	1.387

Table 6 Stream results for Stripper

Variables	RICHIN			LEANOUT			CO2OUT (Tail gas)		
	This Work	Huang et al. ¹²	Rel. Error (%)	This Work	Huang et al. ¹²	Rel. Error (%)	This Work	Huang et al. ¹²	Rel. Error (%)
Temperature (°C)	107	107	0	125.8	127	0.945	30	30	0.0000
Mass Flow (kg/hr)	1127496	1132710	0.460	1045820	1071520	2.398	60580	60770	0.3127
Loading (mol CO ₂ /mol MEA)	0.542	0.550	2.649	0.205	0.20	2.500			
CO₂ flow (kg/hr)							60333	60570	0.3913

4 Improvement of the model

4.1 Rate-based vs. Equilibrium-based model

The Huang et al. ¹² model duplicated above is an equilibrium-based model developed using RadFrac equilibrium model in Aspen Plus[®]. The model is based on theoretical stages. In each stage, liquid and vapor phases reach equilibrium characterized by infinitely fast mass transport. An efficiency factor (e.g., Murphree efficiency) obtained using semi-theoretical models are used to define the separation achieved on each theoretical stage. In reality, equilibrium is rarely attainable, and this imposes a limitation on the ability of the model. In rate-based models, on the other hand, actual mass and heat transfer rate are taken into account. The mass transfer is described using two film theory based on the Maxwell-Stefan formulation (or Fick's Law) with the reaction either modelled kinetically or instantaneously. ²²

Peng et al. ²¹ and Lawal et al. ²² among others have compared the equilibrium-based and rate-based models of reactive columns. Their results showed that rate-based models of reactive columns give a better prediction of the process conditions than the equilibrium-based model. It is therefore concluded that rate-based approach is more suitable for modelling reactive columns such as CO₂ absorption/stripping columns. As a result, the Huang et al. ¹² model duplicated in this study is upgraded using rate-based approach so that the model can potentially become more robust and accurate.

4.2 Rate-based model description

The packing parameters for the absorber and stripper are given in Table 6. Heat and mass transfer correlations are given in Table 7. The columns were initially sized using generalized pressure drop correlation ⁵ alongside data from Huang et al. ¹² The estimated column diameter for the absorber was about 13.78 m. With Aspen estimation using the packing sizing method, a diameter of 13.92 m was obtained, and this validated the manual estimation. The two methods,

manual and Aspen estimation, gives a rough estimate of the column diameter due to some inevitable approximations made during the calculations. As a result, they are subject to some significant level of uncertainty. Starting with the estimated values, different diameters were tried with fixed capture level (90%). It was found that about 10.5 m diameter was a fair compromise between the required 90% capture level and minimum column diameter. A column height of 20 m was chosen for the absorber using the procedure outlined in Lawal et al.⁵ The same methods have been used to determine the stripper diameter and height. After several trials, it is found that a diameter of 9.5 m allows a good rate of CO₂ in the stripper overhead stream (about 99 wt% CO₂) and proper loading of the regenerated solvent.

Table 7 Packing characteristics

Absorber packings			
Type	Vendor	Material	Dimension
IMTP	KOCH	METAL	0.625-IN (16-MM)
Stripper packings			
Type	Vendor	Material	Dimension
FLEXIPAC	KOCH	METAL	1Y

Table 8 Selected correlations in Aspen Plus®

	Absorber	Stripper
Mass transfer and interfacial area prediction	Onda et al. ³⁵	Stichlmair et al. ³⁶
Holdup correlation	Bravo et al. ³⁷	Bravo et al. ³⁸
Heat transfer correlation	Chilton and Colburn ³⁹	Chilton and Colburn ³⁹

5 Process analysis

From comparisons of the mixed solvent (i.e. 30 wt% IL ([Bpy][BF₄]) and 30 wt% MEA given in Table 1) to reference 30 wt% MEA solvent using the rate-based solvent-based capture model, we found like Huang et al.¹² that the mixed solvent reduces the solvent circulation rate and the specific regeneration energy for 90% capture level. However, [Bpy][BF₄] like other ILs is very expensive, about US\$17,160/kg (laboratory scale) based on TCI Chemical pricing (TCI

(<http://www.tcichemicals.com/eshop/en/us/commodity/B3232/>), although Chemical manufacturers such as BASF and Linzhou Keneng Materials Technology Co., Ltd predicted about US\$40/kg⁶ and US\$6.6/kg¹² respectively for industrial-scale production due to economies of scale. Regardless of now or in the future, ILs will remain significantly more expensive compared to MEA which costs about US\$1.250/kg.¹²

Consequently, it is predicted that the mixed solvent formulation using 30 wt% IL as proposed by Huang et al.¹² or higher concentrations as proposed by Camper et al.¹⁸ will lead to significant increase in initial solvent cost compared to 30 wt% MEA solvent. Consequently, a case study is necessary to evaluate process implications of using lower IL concentration in the solvent formulation. Lower IL concentration will ensure that the cost of mixed IL and MEA solvent remains competitive with 30 wt% MEA solvent. Case studies have been developed by varying the concentration of IL in the solvent starting from 0 - 30 wt% in a step of 5 and the impact on different process variables, namely specific regeneration energy, temperature profile and solvent circulation rate were evaluated. The case studies were performed using the improved rate-based model of the solvent-based capture process as described in Section 4.2.

5.1 Setup for the case studies

The setup applies to the case studies described in the following sections. In the case studies, the process was simulated using different aqueous solutions of the solvent as follows:

- 30 wt% MEA and 0 wt% IL (Base case)
- 30 wt% MEA and 5 wt% IL (Case 1)
- 30 wt% MEA and 10 wt% IL (Case 2)
- 30 wt% MEA and 15 wt% IL (Case 3)
- 30 wt% MEA and 20 wt% IL (Case 4)
- 30 wt% MEA and 25 wt% IL (Case 5)
- 30 wt% MEA and 30 wt% IL (Case 6)

The input conditions given in Tables 2 and 3, packing characteristics presented in Table 6 and the column dimensions estimated in Section 4.2 were used in all the cases. The capture level was also fixed at approximately 90% for all the cases.

5.2 Impact of IL fraction on absorber and stripper temperature profile

5.2.1 Justification of the case study

Temperature profiles of the absorber and stripper are useful for understanding heat distribution inside the columns. For the absorber, studies involving 30 wt% MEA solvent⁴⁰ highlighted accumulation of heat at some section in the column leading to a “bulge” in the temperature profile. This was shown in other studies^{31,41-42} to have an adverse impact on the column absorption performance. For the mixed IL and MEA solvent, the temperature profile should be evaluated to understand how it is affected by IL wt%. Insights from the investigation can be useful for designing and installing inter-coolers (for absorber) and inter-heaters (for stripper).

5.2.2 Results and discussions

The absorber profile is presented in Fig .3, **note that the absorber includes a water wash and this is responsible for the unusual behaviour of the profile of the base case (i.e., 30 wt% MEA and 0 wt% IL) at the top region of the absorber as shown in the results.** The solvent temperature for all the cases peaked at a temperature of about 65°C at the same section of the column (Fig. 3) before it begins to decrease reaching about 40°C at the absorber outlet.

The temperature of the base case deviated from other cases (Case 1-6) at the absorber section from 8 m to 20 m. This is attributed to the greater higher heat of reaction released in the base case. Also, the heat capacity of MEA (base case) is smaller than that of the mixed IL and MEA solvent. For instance, at 40°C, the heat capacity of MEA is approximately 161 J/mol K (data from Aspen Plus[®]) compared to 390 J/mol K for [Bpy][BF₄].¹²

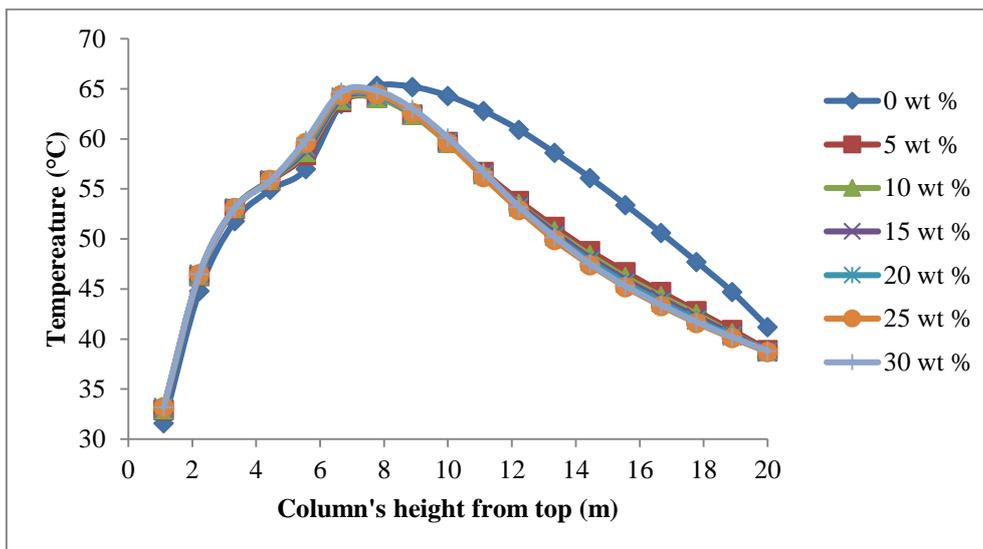


Fig. 3 Impact of IL fraction on absorber temperature profile

For the stripper (Fig. 4), the temperature profile for the mixed solvents deviated less from the base case across the column. The solvent temperature increased as the IL fraction decreased initially to about 3 m down the column. After that, the temperature begins to fall with decreasing IL fraction. The change is less than 5°C except at the tipping point (stripper height = 3 m) where the temperature for the different cases appeared the same.

In summary, IL wt% has minimal impact on the absorber and stripper temperature profile. Absorber temperature bulge issues known with MEA-based solvents (0 wt % of IL) remains an issue with cases involving different amounts of IL.

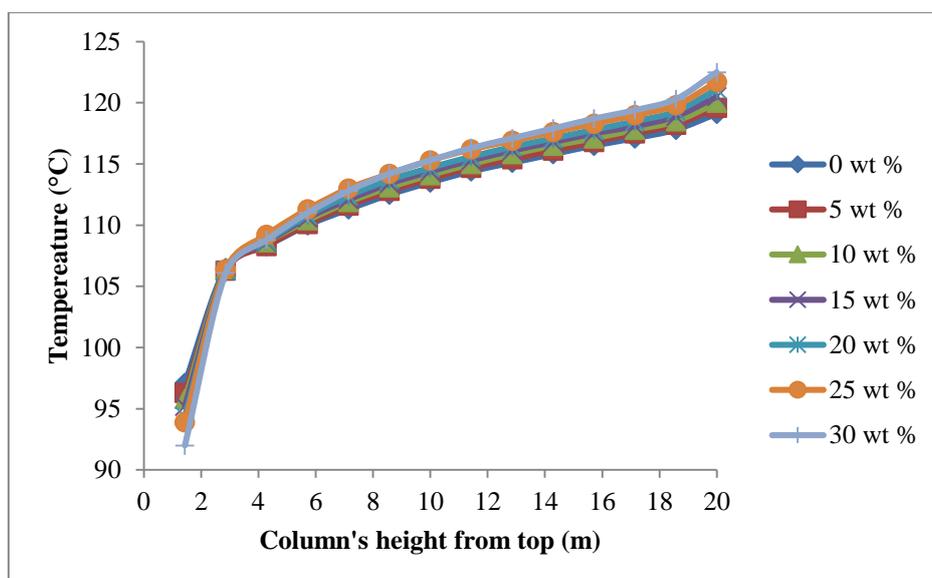


Fig. 4 Impact of IL fraction on stripper temperature profile

5.3 Impact of IL fraction on solvent circulation rate

5.3.1 Justification of the case study

Solvent circulation rate in the solvent-based carbon capture process has a significant impact on equipment sizes, regeneration energy, and overall process economics. For this case study, it is represented in terms of liquid-gas ratio (L/G ratio) (assuming gas flowrate is fixed in all the cases). The impact of changes in IL fraction on L/G ratio is evaluated. The analysis provides insight into the implications of operating with different IL fraction in terms of L/G ratio which will be helpful for selecting appropriate IL fraction in the mixed solvent formulation.

5.3.2 Results and discussions

The results show a reduction in L/G ratio (mol/mol) as IL fraction in the solvent increases (Fig.5). With 5 wt% IL fraction in the solvent formulation, the L/G ratio is reduced by about 11.6%; further increase up to 30 wt% IL fraction achieved approximately 26.8% reduction in the L/G ratio. The decrease is because of higher loading capacity of the solvent with the addition of IL and as such less solvent circulation is required to achieve the target 90% capture level. Comparing the reductions in L/G ratio at different IL concentrations, it is concluded that 5 wt% IL fraction is a good compromise considering the higher cost of IL and reductions in L/G ratio achievable at higher IL fraction. On this basis, it is predicted that the Huang et al.¹² proposed 30 wt% IL fraction in the mixed solvent may not be economically realistic. This is discussed further in Section 6.

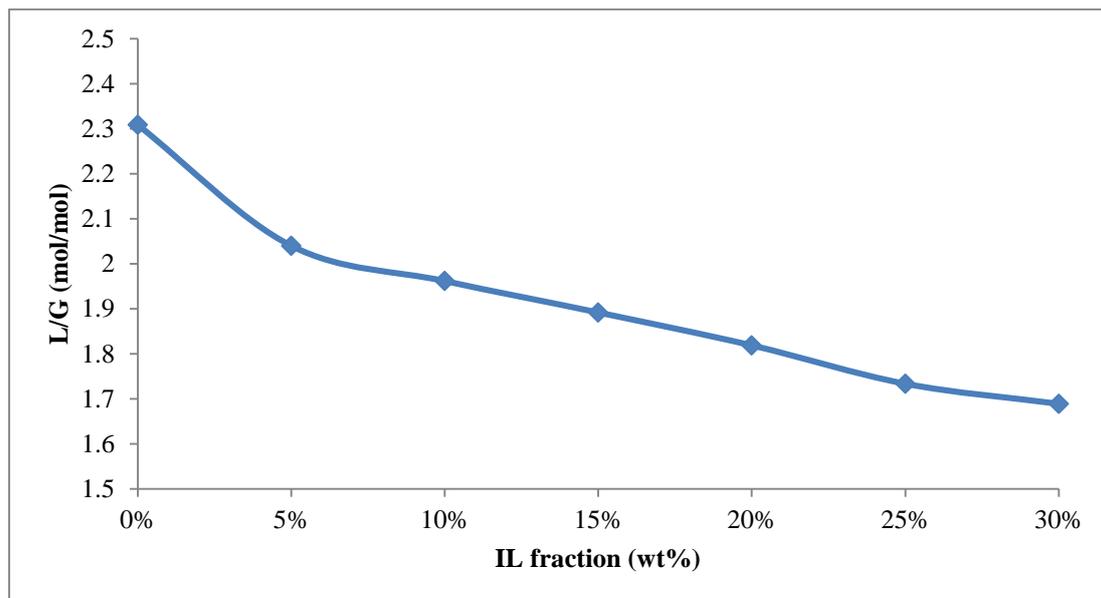


Fig. 5 Impact of IL fraction on L/G ratio

5.4 Impact of IL fraction on regeneration energy

5.4.1 Justification of case study

Regeneration energy is a common metric for assessing the performance of different solvent-based carbon capture processes and the main contributor to overall electricity output penalty for the process when added to a fossil fuel-fired power plant. It is essential to evaluate the impact of different IL fractions on regeneration energy. This will provide a useful benchmark for comparing the performances of mixed IL and MEA solvent with other solvents. Also, the results will be an essential input for determining the suitable IL fraction to use in the combined IL and MEA solvent.

5.4.2 Results and discussions

The results (Fig.6) show that the regeneration energy is lower for the mixed IL and MEA solvent compared to the reference 30 wt% MEA solvent. The regeneration energy reduction is attributed to the following factors: ¹²

- The lower heat capacity of IL-MEA hybrid solvent compared to the reference 30 wt % MEA solution.
- Lower solvent circulation rate as demonstrated in Figure 5

- Reduced vaporization rate due to a smaller amount of water in the mixed IL and MEA hybrid solvent cases.

It is also observed that there is a meaningful reduction in regeneration energy (about 7%) with about 5 wt% IL fraction compared to the base case. Further increase in IL fraction, up to 25 wt%, showed small changes; the more noticeable difference is observed above 25 wt% IL fraction. Using 5 wt% IL fraction appears a good compromise; reductions in regeneration energy at higher IL concentration will not be commensurate with an expected increase in solvent cost.

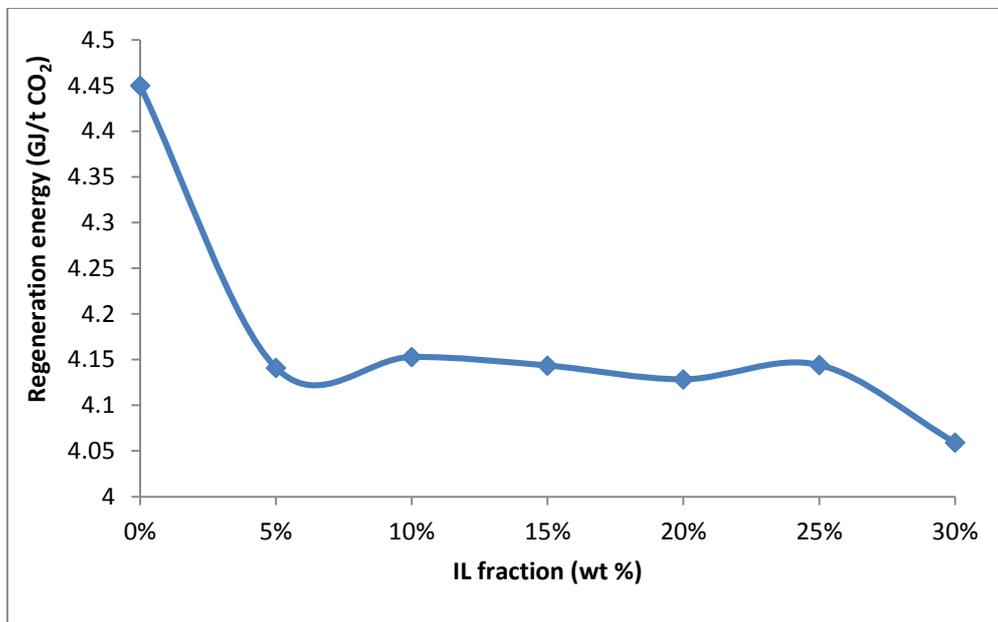


Fig. 6 Impact of IL fraction on regeneration energy

6 Economic analysis

In the economic analysis, only critical variable operating cost, namely solvent makeup cost, steam (for solvent regeneration) cost and the pumping cost (for lean and rich solvent pump) have been considered. The purpose is to demonstrate how different IL concentrations in the mixed solvent affect these vital economic parameters in the process. The capital and fixed operating costs for the process were excluded in our analysis as they have been covered

elsewhere.¹² The economic study was carried out using a combination of data from published articles and Aspen Economic Analyzer (V8.6).

6.1 Solvent make-up cost

The solvent cost estimate is based on water price of US\$4.5/ton, MEA price of US\$1,250/ton and an industrial scale price of US\$6,600/ton for the IL.¹² Current prices of IL, based on lab scale production, are very high (See Section 5). However, different chemical manufacturers (e.g., BASF, Linzhou Keneng Materials Technology Co., Ltd) have predicted that the price of IL will drop drastically with the application of economies of scale in IL production.^{6,12} As a result, the futuristic price estimate has been used as the benchmark for costing the IL. On this basis, the initial circulating solvent cost for IL/MEA solvent is expected to be significantly higher compared to the base case. Due to losses through degradation and fugitive emission, the initial solvent is augmented from time to time to make up for the losses. The solvent make-up cost is routine and reflects in long-term the actual solvent investment cost.

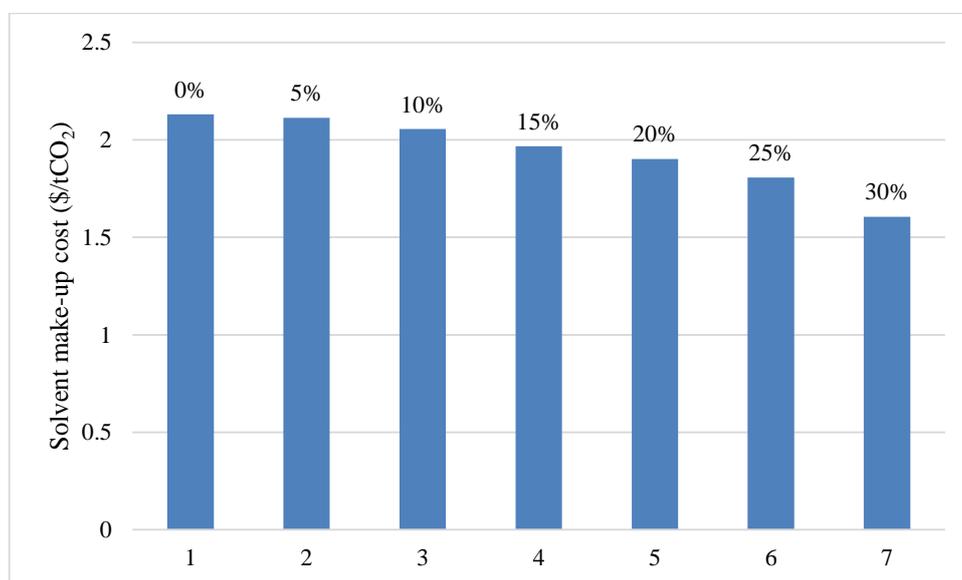


Fig. 7 Solvent make-up cost for different IL wt%

Analysis of the solvent make-up cost using the rate-based model developed in this study shows that makeup cost decreases as IL fraction increases (Fig. 7). This is because of negligible IL

losses due to their better thermal and chemical stability. MEA losses are also less when mixed with IL because of the lower solvent flow rate. In Fig.8, savings that could be achieved as a result of lower make-up cost for different IL concentrations (5-30 wt %) is presented. From the result, it can be seen that there is an exponential increase in savings from solvent make-up as IL wt% in the mixed solvent increases. This result shows that although the initial solvent cost for mixed IL solvent could be significantly higher than the base case as IL wt% increases, the savings from solvent make-up could potentially offset the difference in cost.

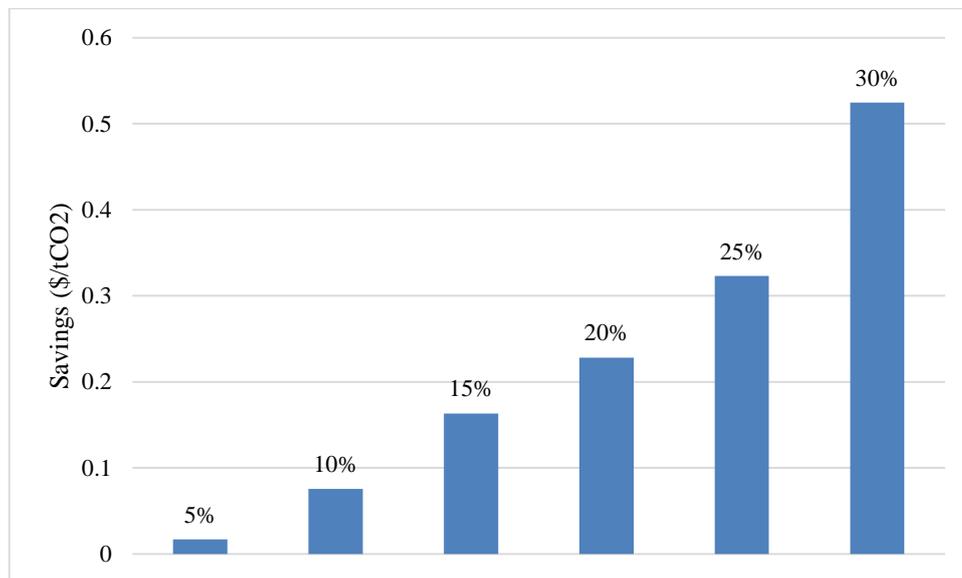


Fig. 8 Savings from solvent make-up for different IL wt% compared with 30 wt% MEA only (i.e., the base case)

6.2 Steam consumption

Steam used for solvent regeneration represents major energy penalty of the solvent-based carbon capture process. The cost of steam consumed for solvent regeneration per ton of CO₂ was estimated for different cases (i.e., 0 – 30 wt % IL concentration). The unit price of steam was estimated as follows (Swagelok Energy Advisor Inc. (https://chicago.swagelok.com/Services/Energy-Services/~/_media/Distributor%20Media/C-G/Chicago/Services/ES%20-%20Knowing%20Cost%20of%20Steam_BP_31.ashx)):

$$S_C = \frac{a_F(H_g - h_f)}{\eta_s} \quad (3)$$

Where:

S_C = unit cost of steam (\$/kg)

a_F = fuel cost in \$/GJ

H_g = enthalpy of steam (kJ/kg)

h_f = enthalpy of feedwater (kJ/kg)

η_s = boiler efficiency

Given that the reference plant is a coke oven plant located in China, the selected fuel is the Luliang (in Shanxi Province) Quasi Grade Coke. The unit price of the fuel (June 2017) is \$228.82/ton (Shanxi Fenwei Energy Information Co., Ltd (<http://en.sxcoal.com/>)) with currency conversion based on 1\$ = 6.56 RMB. The steam is saturated steam at 2bar, and the feedwater temperature is assumed to be 65°C. The boiler efficiency is assumed to be 85%. Based on these assumptions and using Eqn 3, the unit price of steam is \$16.74/ton. The total cost of steam is obtained by combining steam consumed (obtained from the model) and the unit price of steam. The results in Figure 9 show that with the addition of IL, the steam cost decreases by about 6-7% depending on the amount of IL compared to the reference case which indicates a savings of about \$1.5-2 per tonne of CO₂ captured. This is because the steam consumption is roughly lower with IL as discussed in Section 5.4.

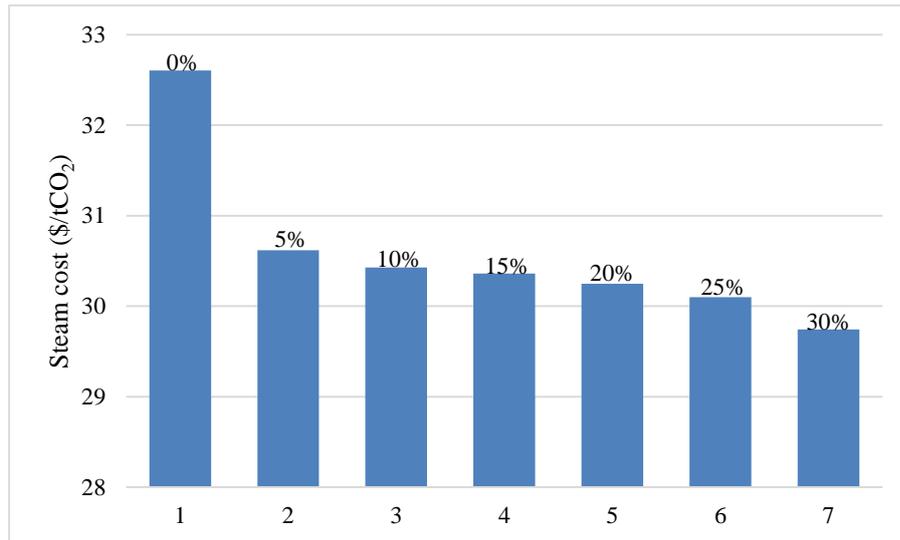


Fig. 9 Steam cost for different IL fractions

6.3 Pumping cost

The pumps (i.e., pumps for lean and rich solvents) and the flue gas inlet blower constitute the primary source of electrical power consumption in the process. The electricity consumption by these unit operations is an essential component of VOPEX in the process. The electricity cost is obtained for the different cases (Section 5.1), and the results were presented in Figure 10. The results indicate an increase in electrical energy consumption as IL fraction in the mixed solvent increases. This is because the solvent density and viscosity increases with IL wt%. The density and viscosity contribute significantly to pumping duties.

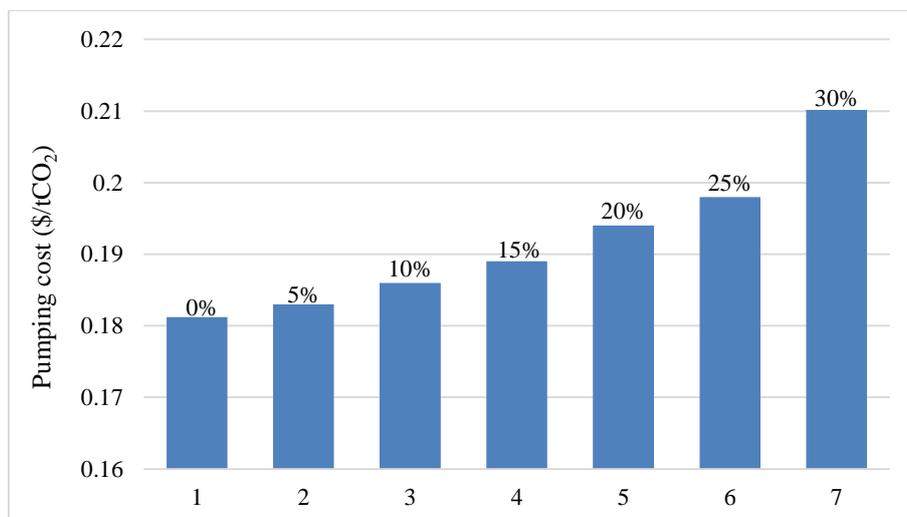


Fig. 10 Pumping cost for different IL fractions

7 Conclusions and recommendations for future research

In this study, comparative assessment of the process and economic performance of using an aqueous mixture of ionic liquid ([Bpy][BF₄]) and MEA as the solvent in a solvent-based carbon capture process for industrial carbon capture is carried out. The study was performed using a rate-based model of the process improved by introducing more accurate and reliable parameters (mainly interaction parameters) in the electrolyte NRTL model used for thermodynamic calculations in the model. The mixed solvent is comprised of an aqueous solution of 30 wt% MEA and different IL fractions (0 – 30 wt%). The aqueous solvent mixtures (5-30 wt% IL) have 7-9% and 12-27% less regeneration energy and solvent circulation rate respectively compared to the base case (Sections 5.4 & 5.5). Based on the predicted cost of IL, the initial solvent cost is predicted to increase significantly as IL wt% in the mixed solvent increases. However, this increase in cost can be offset by savings from solvent makeup cost which increases with IL wt% in the combined solvent. The steam cost was also shown to be less as IL wt% increases. However, pumping cost is slightly more as the IL wt% increases due to higher density and viscosity of the IL. In the future, the entire process using an aqueous mixture of IL and MEA as solvent should be optimized to determine optimal IL wt% in terms of crucial driving process and economic parameters. Also, the rate-based model should be validated using experimental data when the data become available.

Acknowledgement

The authors would like to acknowledge financial support from EU FP7 International Research Staff Exchange Scheme (IRSES) (Reference: PIRSES-GA-2013-612230).

Reference

1. Intergovernmental Panel on Climate Change (IPCC), 2005. IPCC special report on carbon dioxide capture and storage, Cambridge University Press, Cambridge, UK
2. Wang, M., Oko, E. Special issue on carbon capture in the context of carbon capture, utilisation, and storage (CCUS). *Int. J. Coal Sci. Technol.* **4(1)**: 1–4 (2017).

3. Xue, B., Yu, Y., Chen, J., Luo, X., Wang, M. A comparative study of MEA and DEA for post-combustion CO₂ capture with different process configurations. *Int. J. Coal Sci. Technol.* **4(1)**: 15–24 (2017).
4. Kothandaraman, A., Nord, L., Bolland, O., Herzog, H.J., McRae, G.J. Comparison of solvents for post-combustion capture of CO₂ by chemical absorption. *Energy Procedia* **1**: 1373–1380 (2009).
5. Lawal, A., Wang, M., Stephenson, P., Okwose, O. Demonstrating full-scale post-combustion CO₂ capture for coal-fired power plants through dynamic modelling and simulation. *Fuel* **101**: 115-128 (2012).
6. Ramdin, M., de Loos, T. W., T. J.H. Vlucht, State-of-the-Art of CO₂ Capture with Ionic Liquids. *Ind. Eng. Chem. Res.* **51**: 8149–8177 (2012).
7. Thompson, J.G., Frimpong, R., Remias, J.E., Neathery, J.K., Liu, K. Heat stable salt accumulation and solvent degradation in a pilot-scale CO₂ capture process using coal combustion flue gas. *Aérosol and Air Quality Research* **14**: 550–558 (2014).
8. Kittel, J. Gonzalez, S. Corrosion in CO₂ post-combustion capture with alkanolamines-A review. *Oil & Gas Science and Technology- Rev. IFP Energies Nouvelles.* **69 (5)**: 915-929 (2013).
9. Luis, P. Use of monoethanolamine (MEA) for CO₂ capture in a global scenario: Consequences and alternatives. *Desalination* **380**: 93-99 (2016).
10. Boot-Handford, M. E., Abanades, J.C., Anthony, E.J., Blunt, M.J., Brandani, S., MacDowell, N. et al. Carbon capture and storage update. *Energy Environ. Sci.* **7(1)**: 130-189 (2014).
11. Berthod, A. Ruiz-Angel, M.J. and Carda-Broch, S. Ionic liquids in separation techniques *Journal of Chromatography A* **1184**: 6-18 (2008).
12. Huang, Y., Zhang, X. Zhang, X., Dong, H., Zhang, S. Thermodynamic modeling and assessment of ionic liquid-based CO₂ Capture processes. *Ind. Eng. Chem. Res.* **53**: 11805–11817 (2014).
13. Marsh, K.N., Boxall, J.A., Lichtenthaler, R. Room temperature ionic liquids and their mixtures—a review. *Fluid Phase Equilibria* **219**: 93-98 (2004).
14. Zhang, H., Rubin, E. S. Systems Analysis of Ionic Liquids for Post-combustion CO₂ Capture at Coal-fired Power Plants. *Energy Procedia* **63**: 1321 – 1328 (2014).
15. Mac Dowell, N., Florin, N., Buchard, A., Hallett, J., Galindo, A., Jackson, G. et al. An overview of CO₂ capture technologies. *Energy Environ. Sci.* **3**: 1645-1669 (2010).
16. Shiflett, M. B., Drew, D. W., Cantini, R.A., Yokozeki, A. Carbon Dioxide Capture Using Ionic Liquid 1-Butyl-3-methylimidazolium Acetate. *Energy Fuels* **24**: 5781–5789 (2010).
17. Wappel, D., Gronald, G., Kalb, R., Draxler, J. Ionic liquids for Post-Combustion CO₂ absorption. *International Journal of Greenhouse Gas Control* **4 (3)**: 486-494 (2010).
18. Camper, D. Bara, J. Gin, D. L., Noble, R. Room-temperature ionic liquid-amine solutions: Tunable solvents for efficient and reversible capture of CO₂. *Ind. Eng. Chem. Res.* **47**: 8496–8498 (2008).
19. Yang, J., Yu, X., Yan, J., Tu, S.-T. CO₂ capture using amine solution mixed with ionic liquid. *Ind. Eng. Chem. Res.* **53 (7)**: 2790–2799 (2014).
20. Zacchello, B., Oko, E., Wang, M., Fethi, A. Process simulation and analysis of carbon capture with an aqueous mixture of ionic liquid and monoethanolamine solvent. *Int. J. Coal Sci. Technol.* **4 (1)**: 25–32 (2017)

21. Peng, J., Edgar, T.F., Eldridge, R.B. Dynamic rate-based and equilibrium models for a packed reactive distillation column. *Chem. Eng. Sci.* **58**: 2671-2680 (2003).
22. Lawal, A., Wang, M., Stephenson, P., Yeung, H. Dynamic modelling of CO₂ absorption for post-combustion capture in coal-fired power plants. *Fuel* **88** (12): 2455-2462 (2009).
23. Liu, Y., Zhang, L., Watanasiri, S. Representing Vapor–Liquid Equilibrium for an aqueous MEA–CO₂ System using the Electrolyte Non-Random-Two-Liquid model. *Industrial & Engineering Chemistry Research* **38** (5): 2080-2090 (1999).
24. Yan, Y. & Chen, C.-C. Thermodynamic modelling of CO₂ solubility in aqueous solutions of NaCl and Na₂SO₄. *The Journal of Supercritical Fluids* **55** (2): 623-634 (2010).
25. Zhang, Y., Que, H., Chen, C.-C. Thermodynamic modelling for CO₂ absorption in aqueous MEA solution with electrolyte NRTL model. *Fluid Phase Equilibria* **311**: 67-75 (2011).
26. Oko, E., Wang, M. Joel, A.S. Current status and future development of solvent-based carbon capture. *Int. J. Coal Sci. Technol.* **4** (1): 5–14 (2017).
27. Wiley, D.E. and Ho, M.T. The opportunities for reducing CO₂ emission in the iron and steel industry. UKCCSRC Biannual Meeting, Sept. 26-29, 2014, Cardiff UK. Available at: <https://www.slideshare.net/UKCCSRC/dianne-wiley-plenarycardiffbasep14> [Accessed Sept. 2017].
28. Couling, D. J., Bernot, R. J., Docherty, K. M., Dixon, J. K., Maginn, E. J. Assessing the factors responsible for ionic liquid toxicity to aquatic organisms via quantitative structure–property relationship modelling. *Green Chem.* **8**: 82–90 (2006).
29. Docherty, K. M., Dixon, J. K., Kulpa, C. F., Jr. Biodegradability of imidazolium and pyridinium ionic liquids by an activated sludge microbial community. *Biodegradation* **18**: 481–493 (2007).
30. Yunus, N. M., Mutalib, M. I. A., Man, Z., Bustam, M. A., Murugesan, T. Solubility of CO₂ in pyridinium based ionic liquids. *Chem. Eng. J.* **189–190**: 94–100 (2012).
31. Biliyok, C., Lawal, A., Wang, M., Seibert, F. Dynamic modelling, validation and analysis of post-combustion chemical absorption CO₂ capture plant. *International Journal of Greenhouse Gas Control* **9**: 428-445 (2012).
32. AspenTech. (2012) Aspen Physical Property System: Physical Property Methods. Burlington, USA: Aspen Technology, Inc.
33. Huang, Y., Dong, H., Zhang, X., Li, C., Zhang, S. A new fragment contribution-corresponding states method for physicochemical properties prediction of ionic liquids. *AIChE J.* **59**: 1348– 1359 (2013).
34. Canepa, R., Wang, M., Biliyok, C., Satta, A. Thermodynamic analysis of combined cycle gas turbine power plant with post-combustion CO₂ capture and exhaust gas recirculation. *J. Process Mechanical Engineering* **227**(2): 89–105 (2012).
35. Onda K., Takeuchi H., Okumoto Y. Mass transfer coefficients between gas and liquid phases in packed columns. *J. Chem Eng. Jpn* **1**: 56–62 (1968).
36. Stichlmair J., Bravo J. L., Fair J. R. General model for prediction of pressure drop and capacity of countercurrent gas/liquid packed columns. *Gas Sep. Purif.* **3** (1):19-28 (1989).
37. Bravo JL, Rocha JA, Fair JR Mass transfer in Gauze Packings. *Hydrocarb. Process* **64**: 91–95 (1985).

38. Bravo J. L., Rocha J. A., Fair J. R. A Comprehensive model in the performance of columns containing structured packings, distillation, and absorption, Institution of Chemical Engineers Symposium Series 128. *Inst. Chem. Eng.* **1**: PA48–A507 (1992).
39. Knudsen, J. G., Hottel, S.M. H.C., Sarofim, A.F. & Wankat, P. C. and Knaebel, K.S., 1997. Heat and mass transfer. In D. W. Perry, Robert H., Green & J. O. and Maloney, eds. *Perry's Chemical Engineers' Handbook*.
40. Kvamsdal, H. M., and Rochelle, G.T. Effects of the temperature bulge in CO₂ absorption from flue gas by aqueous monoethanolamine. *Ind. Eng. Chem. Res.* **47**: 867-875 (2008).
41. Karimi M., Hillestad M., Svendsen H.F. Investigation of inter-cooling effect in CO₂ capture energy consumption. *Energy Procedia* **4**: 1601-1607 (2011).
42. Ahn, H., Luberti, M., Liu, Z. and Brandani, S. Process configuration studies of the amine capture process for coal-fired power plants. *International Journal of Greenhouse Gas Control* **16**: 29–40 (2013).