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Study of CO₂ removal in natural gas process using mixture of ionic liquid and MEA through process simulation

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Abstract

There has been a shift to less carbon intensive fuels such as natural gas to meet energy demand due to increasing pressure to cut CO₂ emissions. This has prompted a need to assess unconventional and contaminated natural gas reserves (which contains CO₂ concentration of 20mol% or more). The CO₂ capture process with MEA as the solvent is mostly adopted to treat contaminated natural gas. In this study, the option of using a blend of ionic liquids (IL) and MEA as a promising solvent in the process was investigated through modelling and simulation. A detailed rate-based model was developed for both MEA (30wt%) solvent and IL (30wt%)-MEA (30wt%) blend using Aspen Plus® to assess both process and economic performances. The 1-Butylpyridinium ([bpy][BF₄]) ionic liquid was selected in this study. The physiochemical properties of [bpy][BF₄], predicted using Aspen Plus®, showed good accuracy compared with experimental data. The results from this study showed about 15% and 7.44% lower energy consumption in the reboiler duty and CO₂ removal cost respectively with aqueous [bpy][BF₄]-MEA solvent compared to 30 wt% MEA solvent. It is concluded that the aqueous [bpy][BF₄]-MEA solvent is therefore a promising solvent that could replace 30 wt% MEA solvent in this process.

Keywords: *Natural gas processing, CO₂ removal, Chemical absorption, MEA, Ionic liquid, Process simulation*

Abbreviations

ACC	Annual Capital Cost
AOC	Annual Operating Cost
[bpy][BF ₄]	1-butylpyridinium tetrafluoroborate
[bheaa]	Bis(2-hydroxyethyl) ammonium acetate
[bmim][BF ₄]	1-butyl-3-methylimidazolium tetrafluoroborate
[bmim][DCA]	1-butyl-3-methylimidazolium dicyanamide
CW	Cooling Water
DEA	Diethanolamine
DHVLB	Heat of Vaporization at T _b
D&M	Distribution and Marketing
Elec	Electricity
ENRTL	Electrolyte Non-Random Two Liquid
FC-CS	The Fragment contribution – corresponding states
FOC	Fixed Operating Cost
IL	Ionic Liquid
IEA	International Energy Agency
LNG	Liquefied Natural Gas

MDEA	Methyldiethanolamine
MEA	Monoethanolamine
Mis	Miscellaneous
R&D	Research and Development
RK	Redlich Kwong
RKTZRA	Rackett /Campbell-Thodos Mixture Liquid Volume
RTILs	Room temperature ionic liquids
TSILs	Task specific ionic liquids
V_B	Liquid Molar Volume at T_b
VOC	Variable operating cost
VLSTD	Standard liquid Volume

23

Nomenclature

$C_{1i} - C_{3i}$	Equation coefficients for (7)
$C'_{1i} - C'_{3i}$	Equation coefficients for (8)
Z_i^{*RA} and d_i	Equation coefficients for (9)
$A_i - C_i$	Equation coefficients for (10)
$C''_{1i} - C''_{5i}$	Equation coefficients for (11)
$D_i - D_{iii}$	Equation coefficients for (12)
H_{ij}	Henry Constant
P_i^v	Vapour pressure of component i, Pa
P_c	Critical pressure, bar
Q_{reb}	Reboiler duty, kJ/kg _{CO2}
Q_{cond}	Condenser duty, kJ/kg _{CO2}
Q_{cooler}	Cooler duty, kJ/kg _{CO2}
T	Temperature, K
T_b	Normal Boiling temperature, K
T_c	Critical temperature, K
T_r	Reduced temperature, K
V_c	Critical Volume, cc/mol
W_{pump}	Pump power kJ/kg _{CO2}
Z_c	Critical Compressibility factor
σ_i	Surface tension, mN/m

η_i	Liquid Viscosity, cP
ρ_i	Liquid molar density, mol/cc
Ω	Omega
ΔH_f^0	Standard heat of formation, kJ/mol
ΔH_c^0	Standard heat of combustion, kJ/mol
λ_i	Thermal conductivity, kcal-m/hr-m ² -K

24

25 1. Introduction

26 1.1 Background

27 The need to reduce emissions has favoured a shift towards low carbon fuels such as natural gas for
 28 energy generation [1]. It is predicted that a switch to low carbon fuels will contribute about 15% in
 29 expected CO₂ emission cuts by 2050 [2]. Globally, mineable natural gas reserves are far smaller in
 30 comparison to that of carbon intensive fuels (*i.e.* coal) and as such, natural gas supply is less secured
 31 and expensive. This has prompted the need to re-assess the development of unconventional, stranded,
 32 contaminated and sour natural gas reserves [3]. However, raw natural gas is known to contain acid gas
 33 such as CO₂ with concentration of about 20mol% and more, which makes these reserves economically
 34 unviable. These natural gas reserves are predominantly in SE Asia, NW Australia, Central USA, North
 35 Africa and the Middle East [4]. These locations are far from the established gas markets in Western
 36 Europe, Japan and South Korea. Thus, a large amount of natural gas must be conveyed either via long
 37 distance pipeline or as Liquefied Natural Gas (LNG) [3]. The presence of CO₂ in natural gas limits its
 38 quality (heating value) and the liquefaction process performance.

39 Natural gas sweetening technologies are adopted to remove CO₂, so natural gas can meet acceptable
 40 standards for pipeline transport to end-users and/or liquefaction process for LNG [5]. Natural gas
 41 sweetening process involves CO₂ separation from the gas mixture using techniques such as physical
 42 absorption, chemical absorption, adsorption, cryogenic separation and membrane separation among
 43 others [5]. Chemical absorption is the most commonly and widely used separation method in natural
 44 gas sweetening processes [6, 7]. However, it is expensive especially due to the high energy penalty of
 45 the process [8]. Thus, there is a need to explore different options for reducing the high-energy penalty
 46 of the process.

47 1.2 Motivation

48 Amine-based CO₂ absorption/desorption process has been in use for decades in the industry for CO₂
 49 removal from gas mixtures such as natural gas among others [3, 6, 9, 10]. This is primarily due to its
 50 relatively rapid kinetics of the amine solvents [3, 6]. However, amine solvents generally require high
 51 energy for regeneration. They also tend to stimulate equipment corrosion and degrade rapidly during
 52 operation. This makes the operating cost for amine-based process generally high [6]. Thus, attention
 53 has shifted to development of new solvents that have less energy requirement for regeneration and are

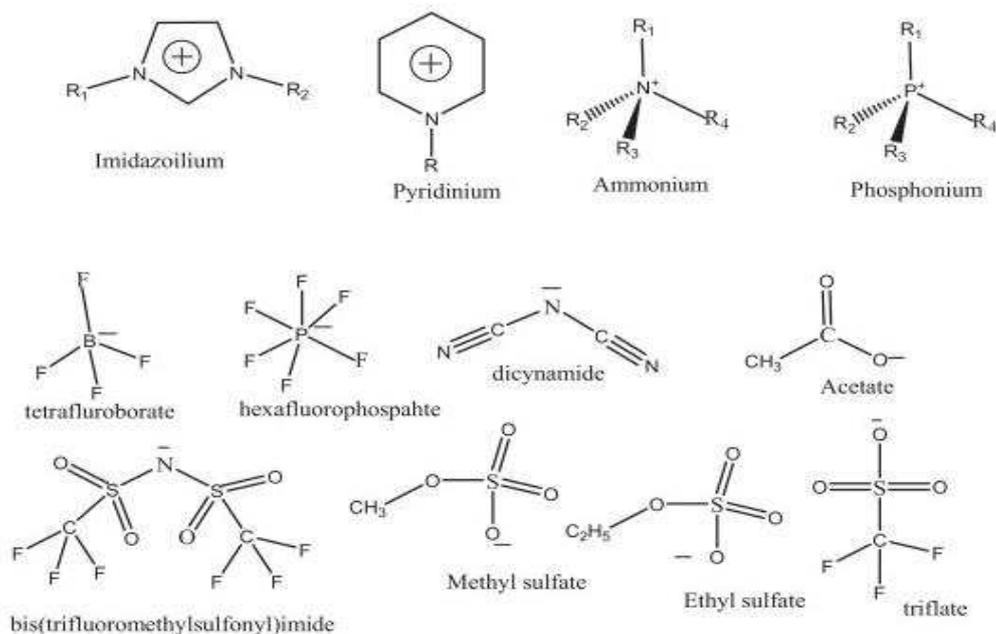
54 more stable, with less tendency to degrade and lower potential for stimulating corrosion. One of such
55 solvents is ionic liquids (ILs).

56 Ionic liquids (ILs) are generally classified as compound composed entirely of ions (cations and anions).
57 They tend to be liquids over a wide range of temperature and are non-volatile which makes them good
58 solvents for a variety of materials. The tunability capability of the ionic liquid makes it possible to tune
59 the ionic liquid structure to suit a specific process requirement by altering either the cation or anion.
60 Some of the commonly encountered cations and anions are shown in Fig.1. ILs requires less energy
61 for regeneration and are environmentally friendly solvents [5]. In addition, they are thermally stable and
62 have low vapour pressure among others. These qualities satisfy the requirements of a more energy-
63 efficient solvent for CO₂ absorption/desorption process than amine solvents [5, 11].

64 Several studies on the properties and application of various ILs for natural gas sweetening and carbon
65 capture through experimental investigations have been carried out [11-18]. From these investigations,
66 it was concluded that the use of ILs only as a solvent is less competitive when compared with MEA.
67 This is due to its low CO₂ absorption capacity. In the quest to find a more competitive solvent, attention
68 has been given to functionalized ILs, supported IL membranes and polymerized ILs [5]. These ILs
69 formulation are considered more expensive than the traditional amine solvents [5]. Also, gas-liquid mass
70 transfer rates are low with ILs due to their high viscosities, resulting in a low reaction rate with CO₂,
71 making them less competitive than amine solvents [5]. These reasons have made IL solvents currently
72 not industrially viable for CO₂ absorption/stripping processes in a large scale [5]. On the other hand, the
73 option of blending ILs and amine solvents have shown a lot of promise [3, 5, 20]. This basically involves
74 merging an eco-friendly IL with the high binding capacity amines [5]. It has been shown that this option
75 requires less regeneration energy than conventional amine process, better process economics and
76 substantially higher gas-liquid mass transfer rates than only ILs [11].

77 1.3 Previous studies

78 Use of IL-Amine blends for natural gas sweetening and carbon capture is driven by the need to develop
79 new solvents with a CO₂ loading capacity comparable to the amine-based solvents and with great
80 reduction in the energy required for regeneration [11]. The section gives a review on the application of
81 IL-amine blends for natural gas sweetening and carbon capture.



82

83 **Fig. 1 General Structure of various cations and anions used for ionic liquid formulation [5]**

84 Various researchers have carried out experimental investigations on the physical properties and
 85 absorption capacity of IL-amine blend. Investigation by Camper et al.[20] on the solubility of CO₂ in IL-
 86 amine blend revealed that the RTIL-amine (RTIL-MEA and RTIL-DEA) blends demonstrated rapid and
 87 reversible CO₂ capture performance, while the amine functionalised TSIL exhibited a slower CO₂
 88 capture performance due to its high viscosity. Similar investigation carried out by Feng et al.[21] showed
 89 that temperature increase enhances the absorption rate. The influence of temperature on the absorption
 90 rate is said to diminish after a long period.

91 study on CO₂ solubility using two ILs blended with MEA ([bheaa]-MEA and [bmim][BF₄]-MEA) by Taib
 92 and Murugesan [22] demonstrated that CO₂ solubility in MEA exhibit chemical solubility while the
 93 solubility of CO₂ in IL exhibits physical solubility, indicating that the CO₂ removal mechanism can both
 94 be physiosorption and chemisorption [23]. Further details on the mechanism analysis for both solvents
 95 can be seen in Taib and Murugesan [22].

96 Experiment studies on CO₂ solubility and physical properties of IL-amine mixture highlighted the impact
 97 of H₂O and amine on the physical properties of the absorbents (particularly density and viscosity),
 98 which enhances CO₂ capture performance [24, 25]. The CO₂ absorption capacity of the IL-amine blend
 99 was mainly a function of amine concentration and the presence of water reduces the IL-amine blend
 100 viscosity, which makes it an industrially viable solvent [24]

101 Further experimental investigation on IL-amine solvent revealed that the hybrid solvent achieved lower
 102 energy consumption compared to conventional solvent [26] and demonstrated better corrosion control
 103 with carbon steel material compared with aqueous amine[27]. More experimental studies on IL-amine

104 solvents can be found in [28-31]. It can be seen that an industrially competitive hybrid solvent could be
105 developed by blending ILs with amine solutions to enhance the CO₂ removal performance.

106 Studies involving whole process analysis of CO₂ removal from gas mixtures using IL-based solvents
107 have also been reported [11, 26]. Despite the successful experimental investigations on the application
108 of IL-amine blends for CO₂ removal, there have been little research on modelling and simulation of the
109 natural gas sweetening process/ carbon capture process using the hybrid solvent to our knowledge. It
110 is necessary that the thermodynamic model adopted accurately predict the hybrid solvent behaviour.
111 This will ensure accurate configuration and operation selection [5]. Huang et al.[32] predicted the critical
112 properties of various IL using the FC-CS method and then carried out thermodynamic modelling,
113 process simulation and cost estimation of CO₂ removal (absorption) process from flue gas (6.37mol%
114 CO₂, 69.46mol%N₂, 3.66mol% O₂, 20.51mol% H₂O) [11]. In the study, three (3) ILs ([bmim][BF₄],
115 [bmim][DCA] and [bpy][BF₄] blended with aqueous MEA solution were investigated. The
116 physicochemical properties of the ILs were predicted by various temperature-dependent correlations.
117 The phase equilibria were modelled based on the Henry's law and NRTL equation. The values
118 calculated agree well with experimental solubility data from literature. From the process simulation
119 assessment, the [bpy][BF₄]–MEA hybrid solvent (with 30wt% IL and 30wt% MEA) process gave savings
120 of 15% and 11% regeneration duty and capture cost compared to the reference MEA based process.
121 Other studies on process analysis of gas mixtures using IL-based solvents includes [33, 34].

122 1.4 Aim and Novelty

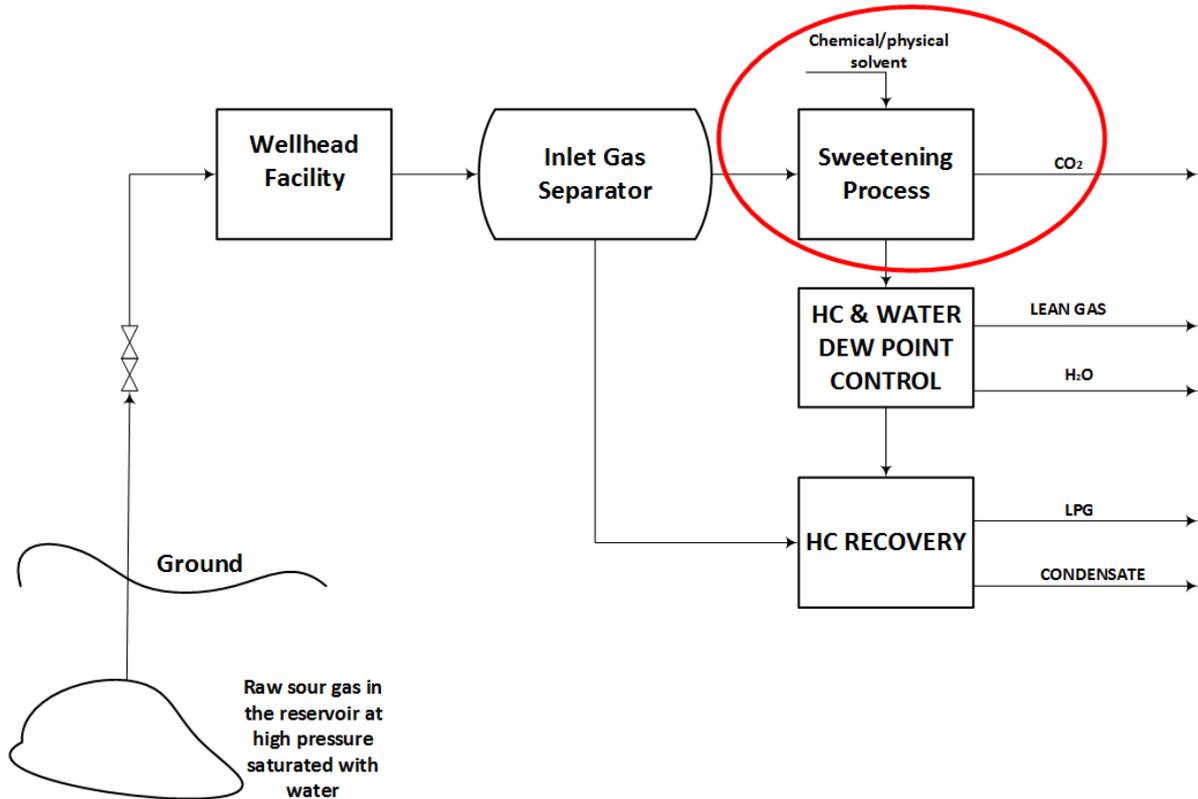
123 The aim of this study is to analyse CO₂ removal from raw natural gas in the context of natural gas
124 sweetening using [bpy][BF₄]-MEA mixture through modelling and simulation. [bpy][BF₄] is selected
125 mainly due to its low cost [19] and low toxicity [35] compared to the imidazolium-based ionic liquids
126 which has been experimentally investigated successfully for removal of CO₂.

127 In carrying out this study, we intend to carry out an energy and cost performance analysis for the IL-
128 MEA process in comparison to the MEA only process. Ionic liquid-amine blends have been reported for
129 CO₂ removal from power plant flue gases by Huang at al. [11]. However, CO₂ removal from natural gas
130 presents a unique scenario involving higher operating pressure (up to 69 bar) and a mixture of light
131 hydrocarbons, namely methane, ethane, propane etc. This will affect the thermodynamics of the
132 process and mass transfer performance and possibly lead to results that are dissimilar to Huang et al.
133 [11]. Thus, it is necessary that a study dedicated to CO₂ removal from natural gas be carried out in the
134 quest to discover a more energy efficient solvent to replace the amine based solvent. Physical
135 properties of the IL in this study were obtained from experimental data available in [13, 15, 17, 36].

136 2. Process benchmark

137 2.1 Description

138 The process schematic for sour natural gas production and processing is shown in Fig.2. In this process,
139 sour gas coming from the production well flows through a separator to knock out condensates in the
140 gas before entering the sweetening process, which is of interest in this study (Fig.3).

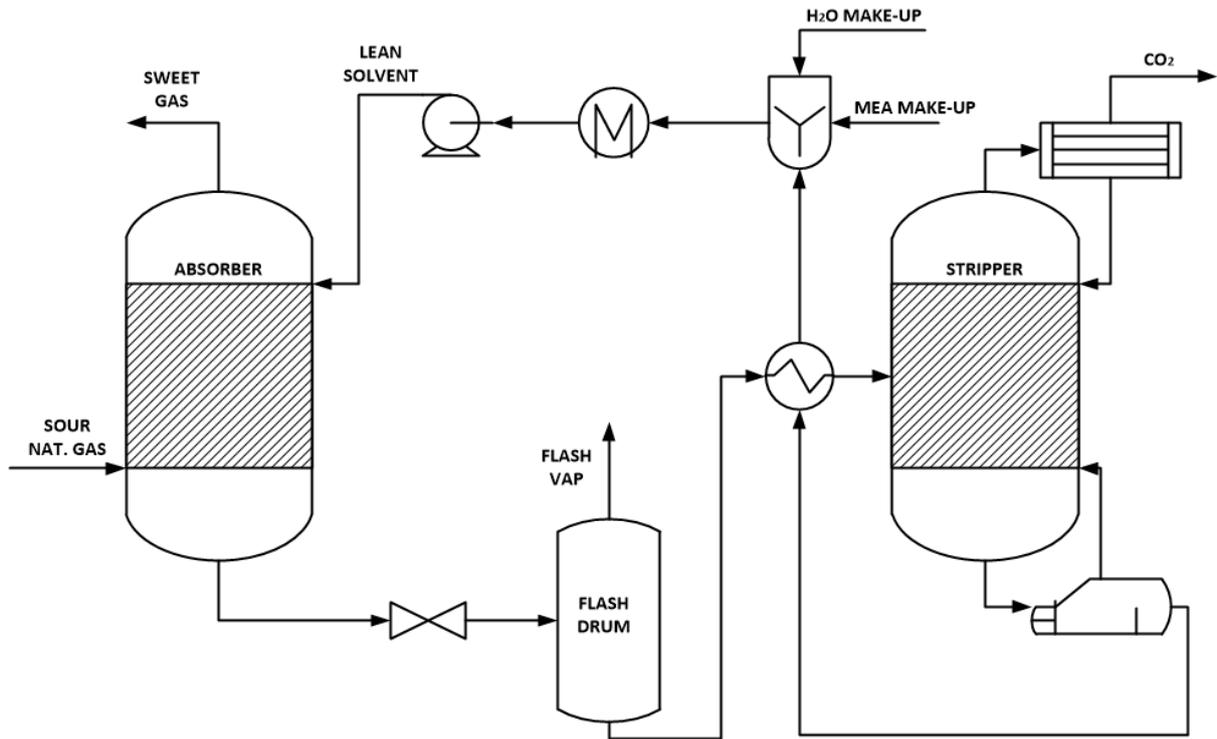


141

142 **Fig. 2 Schematic diagram of sour natural gas production/processing [37]**

143

144 The Natural gas sweetening process mainly consists of absorption and regeneration columns (See
 145 Fig.3). Sour gas (Table 1) flows in the absorber, from the bottom stage. The lean solvent absorbs CO₂
 146 from the sour gas by forming weakly-bonded compounds while flowing in a counter-current manner.
 147 The treated gas exits from the top of the absorber while the CO₂ rich solvent exits from bottom [6, 38].
 148 The rich solvent leaving the absorber, flows to the flash drum to remove absorbed hydrocarbons. The
 149 rich solvent leaves the flash drum to the rich/lean exchanger, where heat is absorbed from the lean
 150 solution. The heated rich solvent flows to the stripper where CO₂ is recovered from the solvent through
 151 heat input to the reboiler. The lean solvent is recycled to the absorber as it flows from the regeneration
 152 column bottom through the rich/lean exchanger, cooler and pump. The process flow diagram shown in
 153 Fig. 3 is adopted for both MEA and hybrid solvent based process.



154

155 **Fig. 3 CO₂ removal process Flow diagram [9]**

156

157 **3. Methodology**

158 3.1 Model Development

159 The absorber and stripper model were developed using RADFRAC model in Aspen Plus®. RADFRAC
 160 supports both equilibrium-based and rate-based approaches for mass transfer modelling. Models based
 161 on both approaches were developed in this study. In the equilibrium-based model, the liquid and gas
 162 phases are assumed to be in equilibrium [39]. On this basis, heat and mass transfer calculations are
 163 then based on estimated efficiency parameters. The rate-based model on the other hand includes
 164 detailed mass transfer calculations based on the two-film theory (Fig.4). The following assumptions
 165 were made during the model development [39]:

- 166 • Mixed flow regime
- 167 • Negligible heat loss to the surroundings
- 168 • N₂ and hydrocarbon not readily soluble in IL and MEA
- 169 • Chemical reactions are completed in the liquid film only

170 **Table 1 Sour Gas Conditions (Obtained from HYSYS [40] with modifications)**

Parameters	Unit	Value
Temperature	°C	35
Pressure	bar	69
Flowrate	MMSCFD (Million Standard cubic feet per day)	25
Component		
Nitrogen	mol%	0.16
Water	mol%	1.22
Methane	mol%	73.76

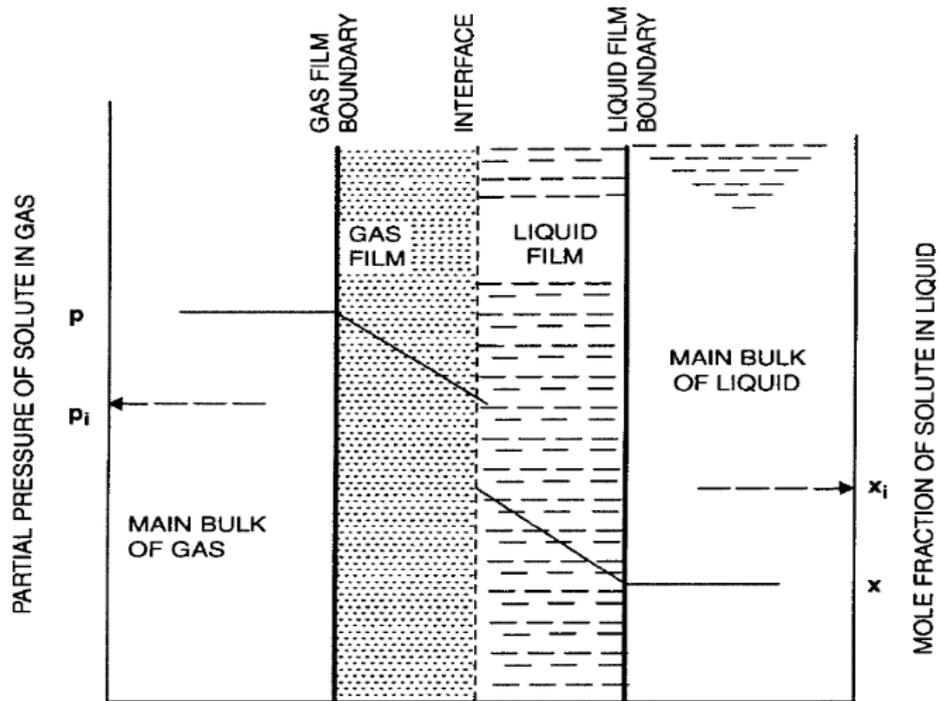
Parameters	Unit	Value
Ethane	mol%	3.93
Propane	mol%	0.93
Carbon dioxide	mol%	20.00

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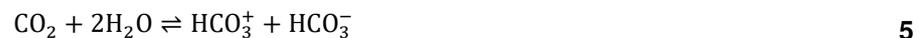
Fig. 4 Two-Film Theory [41]

177

178 3.2 Thermodynamic model

179 3.2.1 CO₂ removal process with MEA

180 Thermodynamic modelling of the conventional CO₂ removal process that involves physicochemical
 181 properties, phase equilibrium and chemical reactions of the component system was carried out using
 182 the Electrolyte Non-Random Two Liquid model (ELECNRTL). The ELECNRTL model is commonly used
 183 for thermodynamic modelling of MEA scrubbing process [11, 39, 42] and has been verified through
 184 industrial applications. The following are the set of chemical reactions considered for the system [6, 9].



185

186 Temperature dependent correlations are used for estimating equilibrium constants as follows:

$$\ln k_j = A + \frac{B}{T} + C \ln T + DT$$

6

187 The reaction equilibrium constants as well as physiochemical properties (both scalar and temperature
188 dependent) of each component, binary parameters and electrolyte pairs were retrieved from the Aspen
189 properties databank.

190 3.2.2 CO₂ removal process using [bpy][BF₄]-MEA

191 3.2.2.1 Physicochemical properties

192 The properties of MEA are available in ASPEN properties databank as previously described. However,
193 there is little information on pyridinium based ionic liquid properties in the databank. Thus, the properties
194 of [bpy][BF₄] were obtained from literature. The scalar properties of [bpy][BF₄] such as the properties
195 were obtained from literature (Table 2). Aspen Plus simulation software was used to estimate other
196 relevant scalar properties of [bpy][BF₄].

197 **Table 2 Scalar properties of [bpy][BF₄] [17, 32]**

Parameters	Unit	Value
T _b	K	697.9
P _c	bar	25.8
ΔH _f ⁰	kJ/mol	-1356.3
ΔH _c ⁰	kJ/mol	-5451

198

199 Temperature dependent properties of [bpy][BF₄] such as heat capacity, molar volume, surface tension,
200 thermal conductivity were obtained using the following equations [11]:

$$\text{Vapour pressure} \quad \ln P_i^v = C_{1i} + \frac{C_{2i}}{T + C_{3i}} \quad 7$$

$$\text{Heat capacity} \quad C_{pi} = C'_{1i} + C'_{2i}T + C'_{3i}T^2 \quad 8$$

$$\text{Molar Volume} \quad V_m^l = \frac{RT_{ci} [Z_i^{*,RA} (1 + d_i(1 - T_r))^{1+(1-T_r)^2}]}{P_{ci}} \quad 9$$

$$\text{Viscosity} \quad \ln \eta_i = A_i + \frac{B_i}{T} + C_i \ln T \quad 10$$

$$\text{Surface tension} \quad \sigma_i = C''_{1i} (1 - T/T_{ci})^{(C''_{2i} + C''_{3i}T_{ri} + C''_{4i}T_{ri}^2 + C''_{5i}T_{ri}^3)} \quad 11$$

$$\text{Thermal conductivity} \quad \lambda_i = D_i + D_{ii}T + D_{iii}T^2 \quad 12$$

201 The Liquid heat capacity is a basic thermodynamic property used for specifying the amount of heat
202 needed to change a liquid temperature by a given amount while the molar volume is a transport property
203 used to describe the volume occupied by one mole of the component at a given temperature and
204 pressure. Given that ionic liquids are well known as a non-volatile liquid whose vapour pressure is
205 difficult to observe [11]. Equation coefficients for (8) to (12) were estimated using data obtained from
206 literature [13, 15, 17, 36] on Aspen Plus® simulation software.

207 3.2.2.2 Phase Equilibria Modelling

208 Generally, the phase equilibrium of the CO₂-H₂O-[bpy][BF₄]-MEA system was based on ELECNRTL
209 model. The electrolyte and interaction parameters of MEA and other components are available in

210 ASPEN properties databank except the pyridinium based IL. The solubility of N₂ in [bpy][BF₄] was
 211 neglected [43]. The phase equilibrium relationship for CO₂ – [bpy][BF₄] system was modelled as follows:

$$\varphi_i^V y_i P = x_i \gamma_i^* H_{ij} \quad 13$$

$$\gamma_i^* = \left(\frac{\gamma_i}{\gamma_i^\infty} \right) \quad 14$$

212 where γ_i^∞ is the infinite dilution activity coefficient of component i in the mixture. Due to the low vapour
 213 pressure of ILs, it is assumed that there will be no IL in the gaseous phase thus, the Henry's law constant
 214 of component i is defined as:

$$H_{ij} = \frac{\varphi_i^V P}{x_i \gamma_i^*} \quad 15$$

215 where H_{ij} , P , x_i , γ_i^* and φ_i^V are Henry constant, total pressure, mole fraction of component i in liquid
 216 phase, activity coefficient of component i in liquid phase and the fugacity coefficient in the vapour phase
 217 respectively. Redlich-Kwong (R-K) equation of state was used to obtain the fugacity coefficient in vapour
 218 phase as follows:

$$\ln \varphi = Z - 1 - \ln(Z - bp/RT) - \left(\frac{a/R^2 T^{2.5}}{b/RT} \right) \ln(1 + bp/ZRT) \quad 16$$

$$Z = pV/RT \quad 17$$

$$p = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)} \quad 18$$

$$a = 0.42748 \frac{R^2 T_c^{2.5}}{P_c} \quad 19$$

$$b = 0.08664 \frac{RT_c}{P_c} \quad 20$$

219 where φ is the fugacity coefficient, Z is the compressibility factor, R is the gas constant, a and b are
 220 equation of state constants. T_c , P_c , V are the Critical temperature, critical pressure and molar volume
 221 respectively. The Henry's constants of component i in mixture j were obtained by using the temperature
 222 dependent henry constants equation shown below [11]:

$$\ln H_{ij} = a_{ij} + b_{ij}/T + c_{ij} \ln T + d_{ij} T \quad 21$$

223 where $a_{ij} - d_{ij}$ are the Henry constant binary interaction parameters. The liquid activity coefficient of CO₂
 224 in the mixture was modelled by the NRTL using (22):

$$\ln Y_i = \frac{\sum_{j=1}^{\delta} x_j x_{ji} G_{ji}}{\sum_{i=1}^{\delta} x_k G_{ki}} + \sum_{j=1}^{\delta} \left(\frac{x_j G_{ij}}{\sum_{k=1}^{\delta} x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_{m=1}^{\delta} x_m \tau_{mj} G_{mj}}{\sum_{k=1}^{\delta} x_k G_{kj}} \right) \right) \quad 22$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$$

$$\tau_{ij} = a_{ij} + b_{ij}/T + e_{ij} \ln T + f_{ij} T$$

$$\alpha_{ij} = c_{ij} + d_{ij}(T - 273.15)$$

$$\tau_{ii} = 0; G_{ii} = 1; c_{ij} = 0.3$$

225 where a_{ij} , b_{ij} , c_{ij} , d_{ij} , e_{ij} and f_{ij} are the binary interaction parameter, δ is the number of components
 226 and x is the mole fraction. The parameters of Henry constants and NRTL binary interaction parameters
 227 between CO₂ and [bpy][BF₄] generated by Huang et al. [11] were inputted in ASPEN Plus® simulation
 228 software. The parameters have been validated in Huang et al. [11].

229 For the H₂O-[bpy][BF₄]-MEA system, VLE calculation was carried out based on the modified Raoult's
 230 law as follows:

$$y_i p = x_i \gamma_i p_i^v \quad 23$$

231 Based on the assumption that the vapour mole fraction of [bpy][BF₄] is negligible, (23) is simplified into
 232 the following equations for both H₂O-[bpy][BF₄] and H₂O-[bpy][BF₄]-MEA;

$$p = x_a \gamma_a p_a^v \quad 24$$

$$p = x_a \gamma_a p_a^v + x_c \gamma_c p_c^v \quad 25$$

233 where subscripts "a" and "c" denotes H₂O and MEA respectively. [9] obtained the binary parameters of
 234 [bpy][BF₄]-H₂O and [bpy][BF₄]-MEA system from experimental data based on (24) and (25) in
 235 combination with NRTL model (22). These binary parameters obtained were used in this study.

236 3.3 Process Simulation

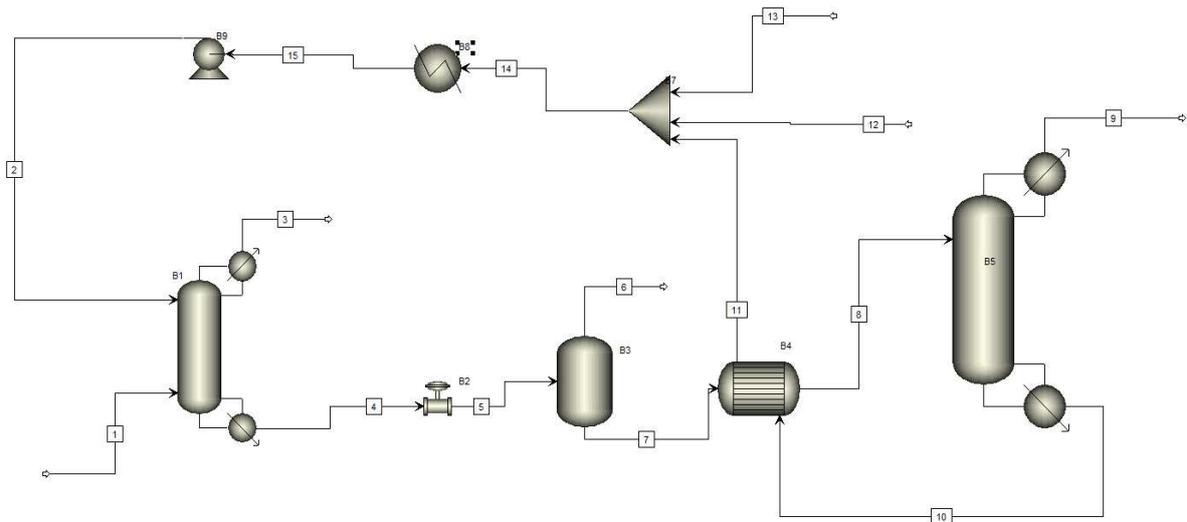
237 Acid gas sweetening process models using aqueous MEA solvent and aqueous [bpy][BF₄]-MEA solvent
 238 were developed in Aspen Plus®. The composition of the solvents for each process are shown in Table
 239 3. The Equilibrium based approach was basically adopted to estimate the column sizes. Under rate
 240 based approach, Bravo et al.[44] correlation was used to estimate the mass transfer coefficient and
 241 Interfacial area while the Chilton and Colburn correlation was used to estimate the heat transfer
 242 coefficients. Equipment specifications used in the process simulation are detailed in Table 4. The model
 243 topology is given in Fig.5.

244 Both process models were simulated to achieve 1 mol% of CO₂ at the absorber gas outlet and 95 wt%
 245 CO₂ concentration recovered from the stripper by manipulating the lean solvent flowrate and reflux ratio.

246 **Table 3 Components and composition**

MEA		
H ₂ O	wt%	70
MEA	wt%	30
IL-MEA		
H ₂ O	wt%	40
MEA	wt%	30
[Bpy][BF ₄]	wt%	30

247



248

249 **Fig. 5 Process model topology in ASPEN Plus®**

250

251 **Table 4 Base specifications of each Unit Operation**

Unit Operation Specification		Unit
Absorber		
Theoretical stages number	20	
Column height	6	meter
Top stage Pressure	6860	kPa
Packing Type	FLEXIPAC	
Packing dimension	250Y	
Packing material	Metal	
Flash tank		
Pressure	620	kPa
Heat Exchanger		
Hot/Cold outlet temperature approach	5	°C
Hot side pressure drop	0	kPa
Stripper		
Number of stages	20	
Condenser	Partial-vapour	
Top stage pressure	170	kPa
Column pressure drop	0.1	kPa
Column height	6	meter
Packing Type	FLEXIPAC	
Packing dimension	250Y	
Packing material	Metal	
Cooler		

Unit Operation Specification		Unit
Temperature	38	°C
Pump		
Discharge pressure	6860	kPa

252

253 3.3.1 Energy performance

254 The specific (reboiler) heat duty is a critical parameter to measure performance in the CO₂ removal
 255 process. The specific heat duty measures heat required in the reboiler to remove 1tonne of CO₂. In this
 256 study, the energy consumption from the energy utilizing equipment (pump and reboiler) were
 257 considered to measure the energy performance of both MEA and [Bpy][BF₄]-MEA based process. For
 258 the reboiler, it is assumed that steam is supplied from the steam boiler at a pressure of 3 bar to achieve
 259 reboiler temperature specification (120°C).

260 3.3.2 Cost Analysis

261 The cost of CO₂ removed for both process, which depends on the annual capital and operational cost,
 262 was estimated based on the breakdown adopted in [11, 45]. The equipment size selection and costing
 263 was carried out using Aspen Process Economic analyzer software, based on the first quarter of 2013
 264 chemical engineering plant cost index (CEPCI). The annual capital cost (ACC) is calculated as:

$$ACC = \frac{TCC}{((1 + r)^n - 1)/r (1 + r)^n} \quad 26$$

265 where TCC is the total capital cost with an interest rate (r) and project lifetime (n) of 20% and 30years
 266 respectively. A breakdown of the total capital and operational cost (fixed and variable cost) components
 267 following [11, 45, 46] is detailed in Table 5. The cost of MEA and pyridinium based ionic liquid solvents
 268 adopted for this study was 0.93 GBP/kg (1.25 USD/kg) and 4.88 GBP/kg (6.6 USD/kg) respectively [11,
 269 47].

270 **Table 5 Cost Estimation Breakdown**

Capital Cost Breakdown	(%) of Equipment Cost (EC)
Installed Cost	10% of EC
Instrumentation and Control	20% of EC
Piping	30% of EC
Electrical	5% of EC
Building and building Services	10% of EC
Yard Improvements	10% of EC
Land	5% of EC
Miscellaneous	2% of EC
Direct Cost (DC)	Sum of the above
Engineering and Supervision (E&S)	15% of DC
Contingency (C)	11% of DC

Procurement Cost (PC)	2% of DC
Indirect Cost (IDC)	E&S + C + PC
Fixed Capital Cost (FCC)	DC + IDC
Working Capital (WC)	15% of FCC
Start-up Cost (SC)	1% of FCC
Initial Solvent Cost (ISC)	Solvent circulation x cost
TCC	FCC + WC + SC + ISC
Operating Cost Breakdown	
Steam Utility Cost (£/GJ)	1.63
Cooling water Utility Cost (£/GJ)	0.157
Electricity Utility Cost (£/kWhr)	0.057
Make-up water Cost (£/kg)	0.00037
Make-up MEA Cost (£/kg)	0.925
Make-up IL Cost (£/kg)	4.884
Miscellaneous operating cost	2% of VOC
VOC	Sum of the above cost
FOC	Sum of the below cost
Local Tax (LT)	1% of FCC
Insurance	1% of FCC
Maintenance (M)	3% of FCC
Operating Labour (OL)	£ 26.64 per hr
Lab Costs	20% of OL
Supervision	20% of OL
Plant Overheads	50% of OL
Operating Supplies	15% of M
Admin Cost	15% of OL
Distribution and Marketing	0.5% of OC
R&D Cost	5% of OC
Operating Cost (OC)	VOC + FOC

271 3.3.3 Process Analysis

272 Analysis on the impact of pyridinium based ionic liquid concentration on the energy and cost
273 performance of hybrid solvent-based process was carried out. The mass fraction of [bpy][BF₄] in the
274 hybrid solvent was varied while keeping the mass fraction of MEA constant. For each case considered,
275 the process was simulated to achieve 1 mol% of CO₂ at the absorber gas outlet and 95 wt% CO₂
276 concentration recovered from the stripper at minimum energy consumption.

277 **4. Physiochemical Property Validation of [bpy][BF₄]**

278 Scalar properties and the coefficients of temperature dependent properties of [bpy][BF₄] estimated
 279 using Aspen Plus® simulation software are listed in Tables 6 and 7. The temperature dependent
 280 properties estimated by Aspen Plus® gave a good prediction when compared with the experimental
 281 data retrieved from literature as shown in Fig.6.

282 **Table 6 Scalar Property Parameters of [bpy][BF₄]**

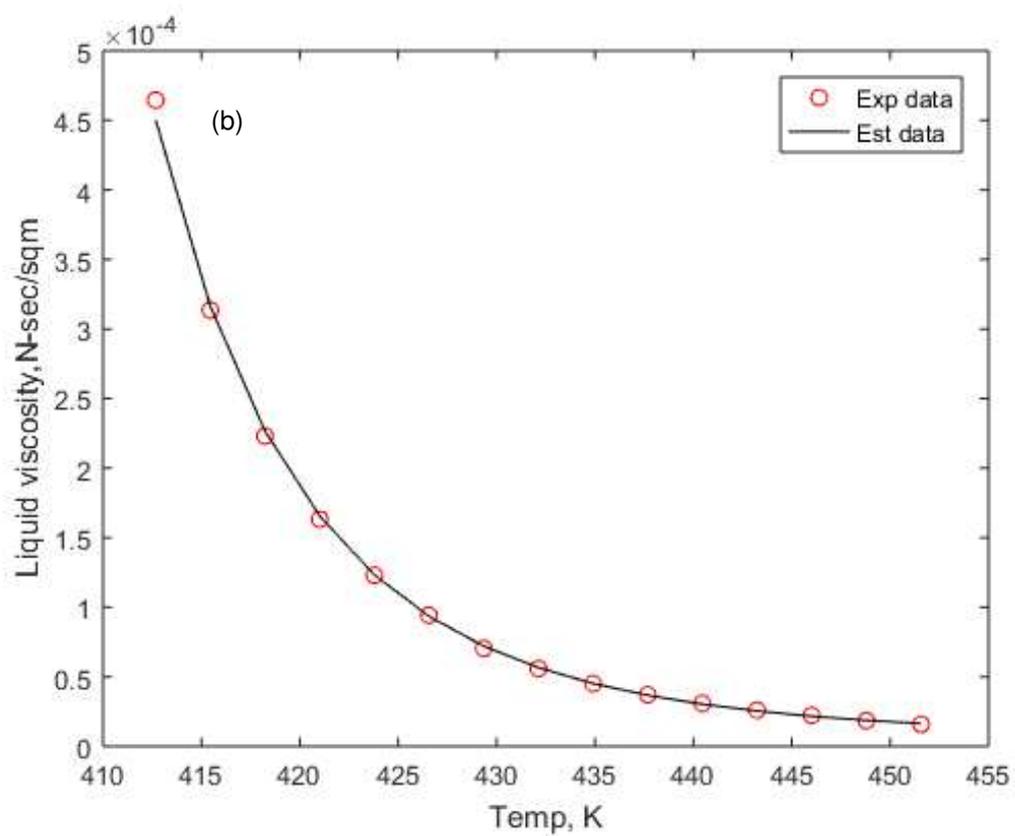
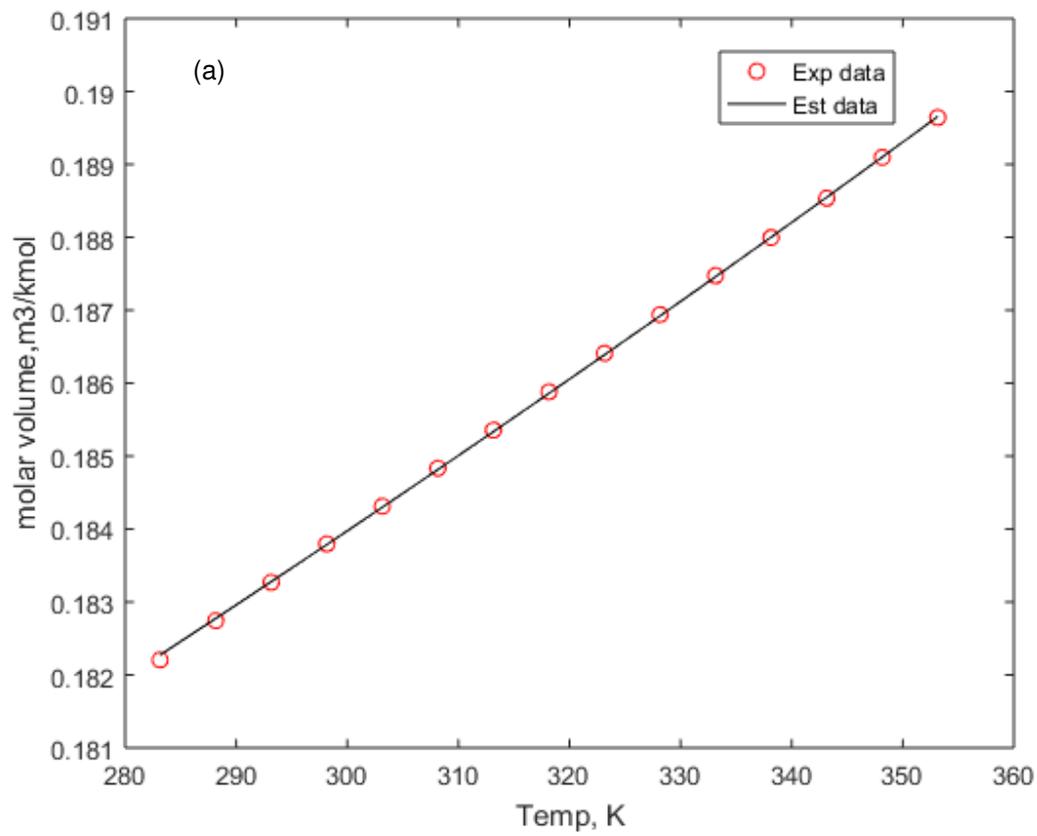
T _C	°C	723.81
DHVLB	J/kmol	6.54E+07
V _B	m ³ /kmol	0.23
RKTZRA		0.22
VLSTD	m ³ /kmol	0.18
V _C	m ³ /kmol	0.82
Z _C		0.26
P _C	bar	25.8

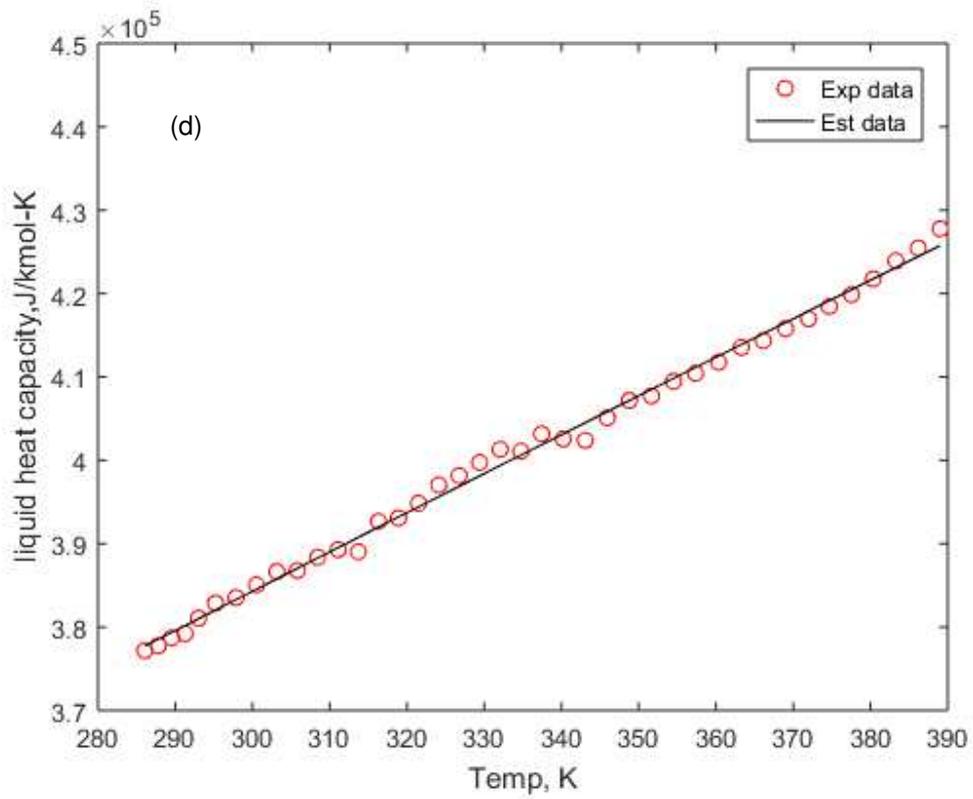
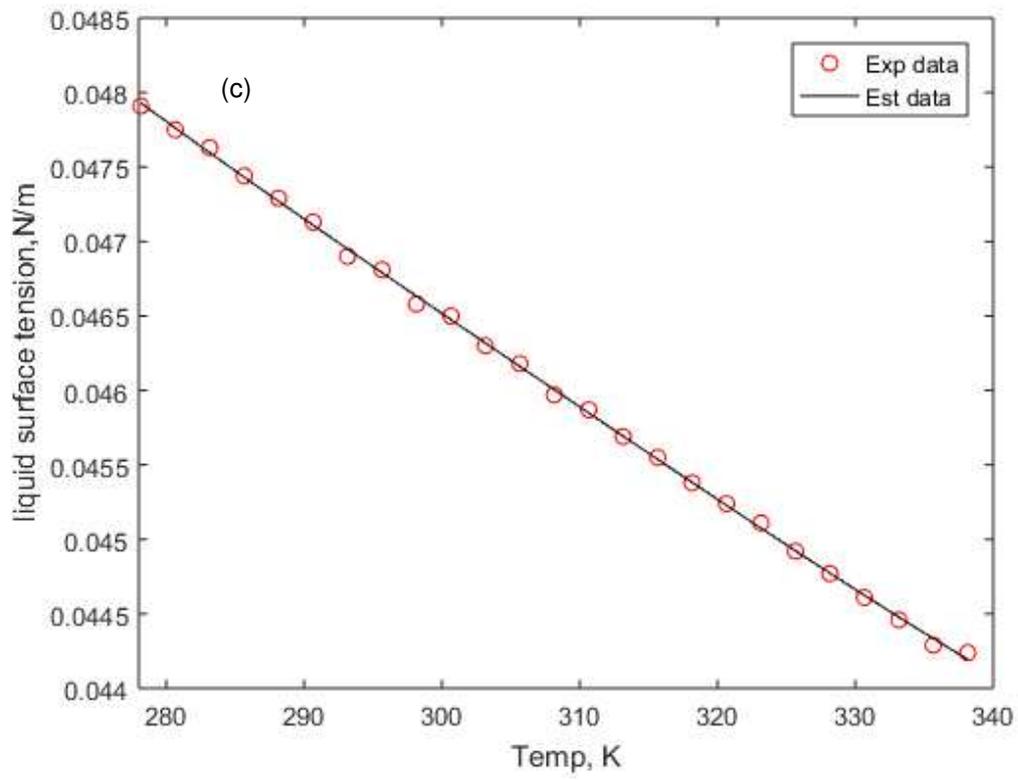
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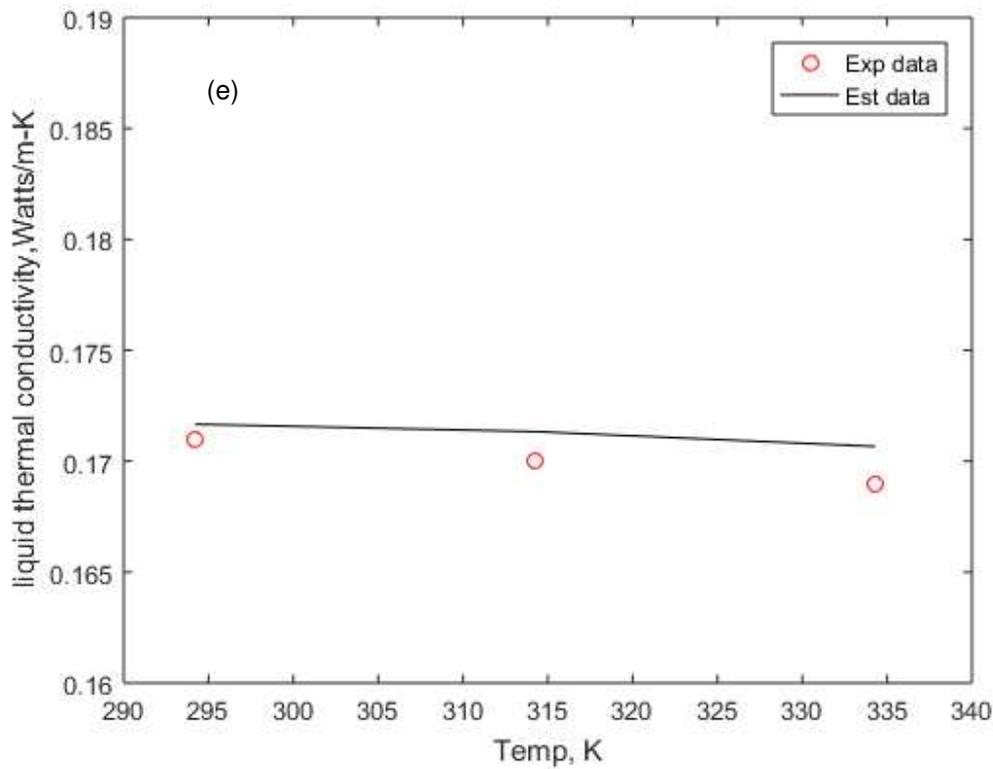
Table 7 Temperature dependent parameter for [bpy][BF₄]

Liquid Viscosity (N-sec/m²)	
A _i	-2.435E+03
B _i	1.618E+05
C _i	3.380E+02
Liquid Surface Tension (N/m)	
C'' _{1i}	7.040E+01
C'' _{2i}	8.819E+01
C'' _{3i}	-4.431E+02
C'' _{4i}	9.597E+02
C'' _{5i}	-7.821E+02
Liquid thermal conductivity (W/m-K)	
D _i	1.292E+01
D _{ii}	2.453E+04
D _{iii}	3.949E-08
D _{iiii}	-2.020E-09
D _{iiiii}	2.441E-12
Liquid heat Capacity (J/kmol-K)	
C' _{1i}	-2.435E+03
C' _{2i}	1.617E+05
C' _{3i}	3.380E+02

287







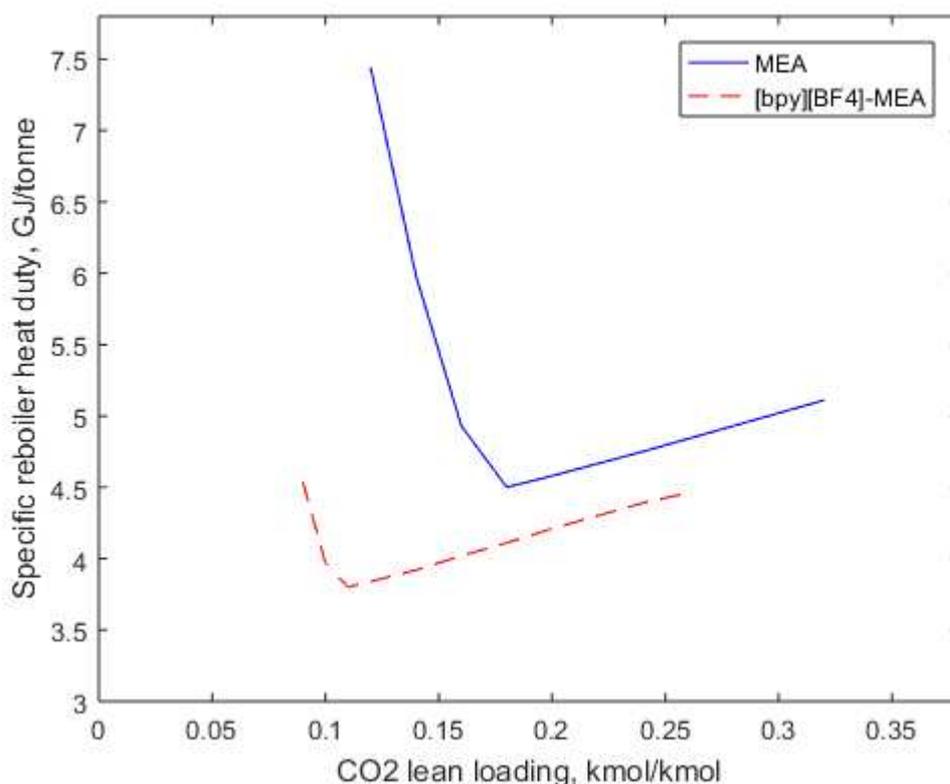
288 **Fig. 6 Temperature dependent properties prediction for [bpy][BF₄] using Aspen Plus (a) molar**
 289 **volume (b) liquid viscosity (c) liquid surface tension (d) liquid heat capacity (e) liquid thermal**
 290 **conductivity; circles and lines denoted experimental data from literature and estimated data [13,**
 291 **15, 17, 36] respectively.**

292 **5. Performance comparison of MEA and [bpy][BF₄]-MEA process**

293 Performance evaluation of both MEA-based and [bpy][BF₄]-MEA-based process was based on the
 294 following performance index: energy performance, mass transfer within the absorber, make-up solvent
 295 required, cooling water and CO₂ removal cost. The summary of results for both process simulation is
 296 shown in Table 8.

297 **Table 8 key parameters result summary**

Process Parameters	Unit	MEA	[bpy][BF ₄]-MEA
lean solvent flowrate	kg/hr	122931	129737
L/G	kg/kg	4.37	4.61
CO ₂ lean loading	kmol CO ₂ /kmol solvent	0.18	0.11
CO ₂ Rich loading	kmol CO ₂ /kmol solvent	0.59	0.42
rich solvent temperature	°C	80	76
Reboiler temperature	°C	120	126
Specific heat duty	GJ/tonne CO ₂	4.50	3.80
Pump Duty	GJ/tonne CO ₂	0.12	0.11
Cooling Water	tonne/hr	1958.59	1398.71
Make-up Solvent	kg/tonne CO ₂	33.28	32.91



298

299 **Fig. 7 Effect of CO₂ lean loading on the specific reboiler heat duty requirement of MEA and**
 300 **[bpy][BF₄]-MEA.**

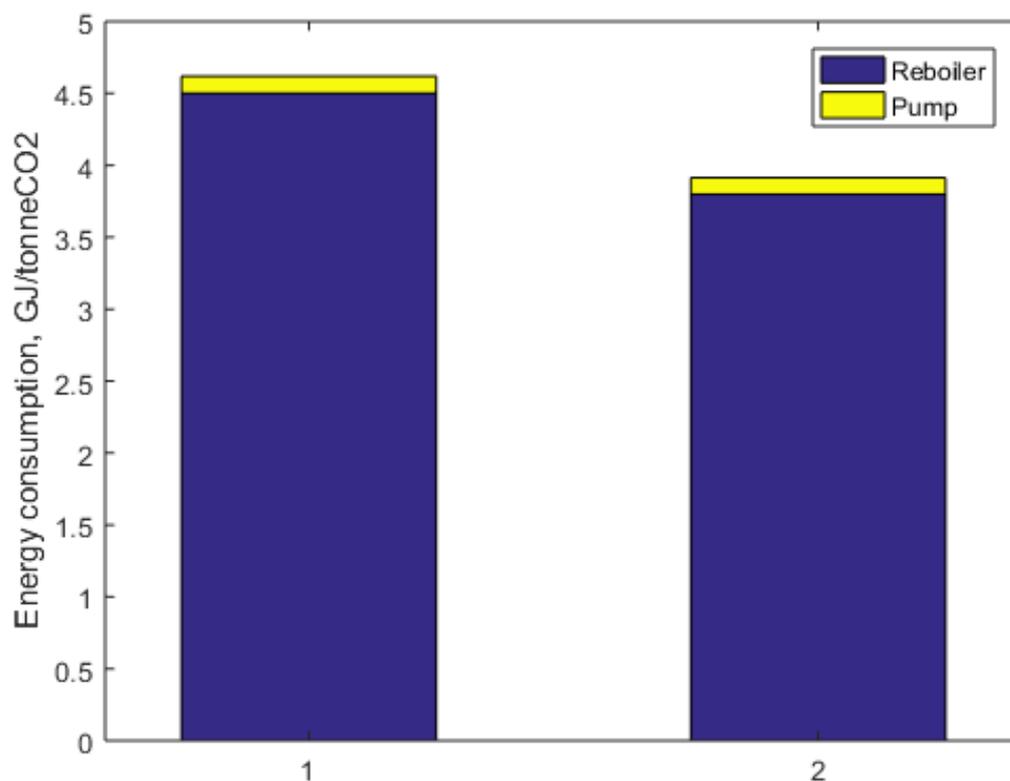
301

302 5.1 Energy performance

303 The specific heat duty of MEA and [bpy][BF₄]-MEA process was evaluated by varying CO₂ lean loading
 304 to achieve the minimum specific heat duty. The CO₂ loading with minimum specific heat duty for both
 305 process were compared. Fig. 7 shows the specific reboiler heat duty plot as a function of CO₂ loading.
 306 It can be seen that the specific heat duty decreases with increasing CO₂ loading until it gets to its
 307 minimum, and then a steady rise in the specific heat duty is observed as CO₂ loading is increased
 308 further. This is because at low CO₂ loading, the heat duty is mainly governed by the latent heat of
 309 vaporization. The latent heat reduces as the CO₂ loading is increased until it is constant. The sensible
 310 heat begins to have a dominant effect on the heat duty due to the increase in the solvent circulation
 311 flowrate. The minimum specific heat duty was attained at a CO₂ loading of 0.18 for MEA process and
 312 0.11 for [bpy][BF₄]-MEA based process.

313 It was observed that the specific heat duty required for [bpy][BF₄]-MEA based process (3.8GJ/tonne)
 314 is less than that required for a MEA based process (4.5GJ/tonne). This is attributed to reduction of latent
 315 heat and heat capacity of the hybrid solvent in a reboiler. The reduced latent heat is as a result of
 316 reduced concentration of water to vaporize in the hybrid ([bpy][BF₄]-MEA) solvent. The presence of
 317 [bpy][BF₄] in the hybrid solvent reduces the heat capacity despite an increase in the solvent circulation
 318 flowrate.

319



320

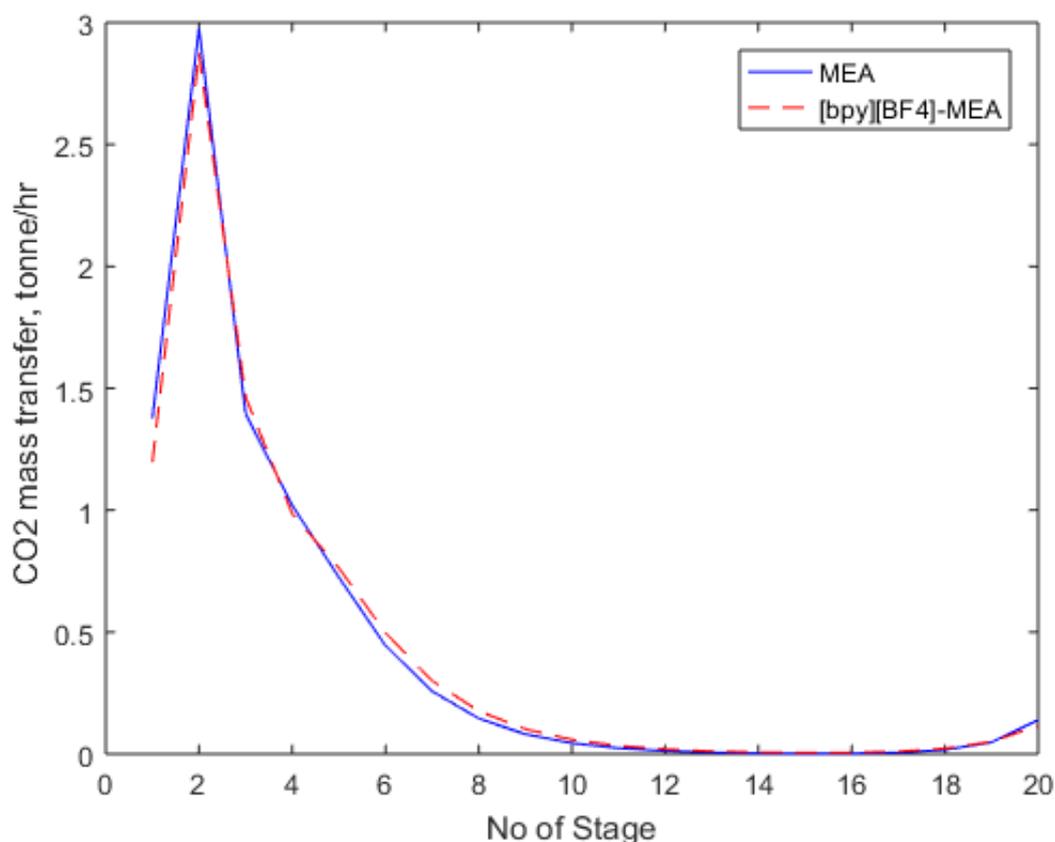
321 **Fig. 8 Energy Consumption for MEA (1) and [bpy][BF₄]-MEA (2) based process**

322

323 The energy consumption for each process is shown in Fig.8. This takes into consideration pump duty
 324 in addition to the specific heat duty. It can be seen from Fig.8 that the reboiler accounts for the largest
 325 share of energy consumed in both MEA and [bpy][BF₄]-MEA process. From Table 8, the pump duty
 326 required for the hybrid process is slightly similar compared to the MEA based process. This is because
 327 solvent circulation flowrate required for [bpy][BF₄]-MEA based process is similar compared to the MEA
 328 based process with a percentage difference of 5.54%. The [bpy][BF₄]-MEA based process is shown to
 329 be more energy saving in the reboiler by 15 % than the conventional MEA based process.

330 5.2 Mass Transfer

331 The mass transfer performance of both process was evaluated by plotting the mass transfer rate of CO₂
 332 from the vapour phase to liquid phase in the absorber. As shown in Fig.9, both process gave a similar
 333 mass transfer performance. Despite this, it was observed from Table 8 that the solvent circulation rate
 334 for the MEA based process is slightly reduced by 5.54 % compared to the [bpy][BF₄]-MEA based
 335 process to achieve the same CO₂ removal specification. This is attributed to the high viscosity,
 336 molecular weight and density of the [bpy][BF₄]-MEA solvent compared with MEA.



337

338 **Fig. 9 CO₂ mass transfer rate (kmol/hr) in the Absorber for MEA and [bpy][BF₄]-MEA based**
 339 **process**

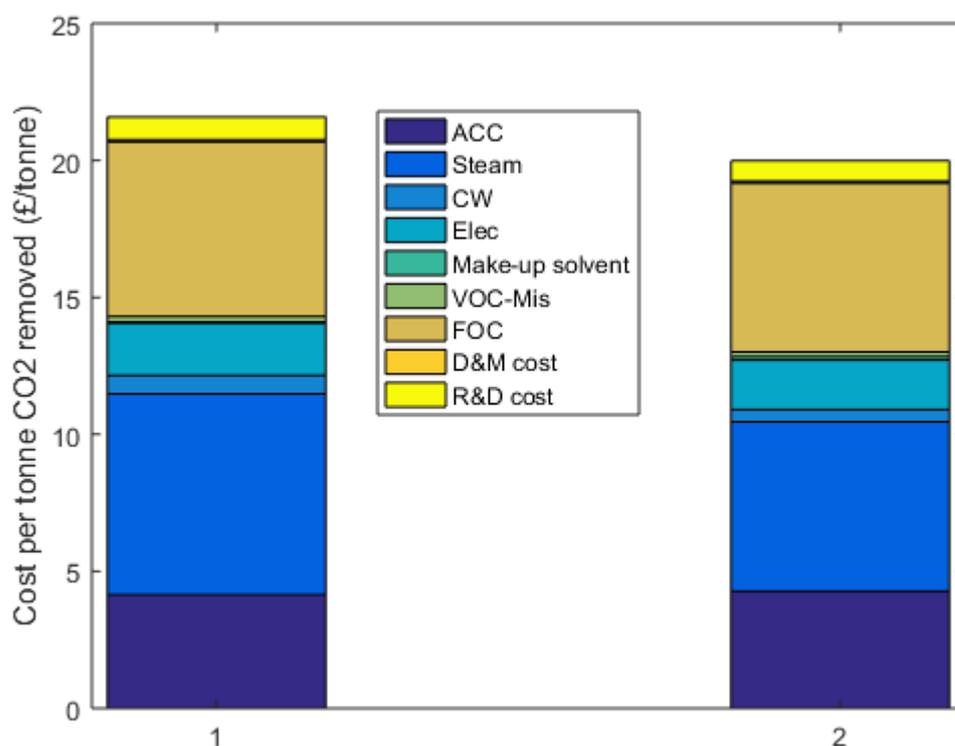
340

341 5.3 Make-up Solvent

342 The make-up solvent is measured as the kg of solvent per tonne of CO₂ removed. From Table 8, the
 343 make-up solvent needed for the [bpy][BF₄]-MEA process is slightly lower than make-up needed for MEA
 344 process. The make-up solvent is composed of mainly MEA and H₂O. This is basically due to the low
 345 vapour pressure of [bpy][BF₄], which reduces degradation of the ionic liquid. Thus making make-up for
 346 [bpy][BF₄] negligible.

347 5.4 Cooling Water

348 The cooling water required for [bpy][BF₄]-MEA based process and MEA based process takes into
 349 consideration the cooling water required in condenser and cooler. The [bpy][BF₄]-MEA process requires
 350 less cooling water required compared with MEA process. The reduced amount of water vaporized in
 351 the stripper reduces cooling water required in the condenser duty to achieve CO₂ purity specification.
 352 The cooling water required in the cooler is reduced for the [bpy][BF₄]-MEA based process due to the
 353 increased temperature of the inlet stream to the cooler.



354

355 **Fig. 10 Breakdown of the Cost of CO₂ removed for (1) MEA-based process and (2) [bpy][BF₄]-**
 356 **MEA based process**

357

358 5.5 Cost Analysis

359 A breakdown of the cost of CO₂ removed is shown in Fig.10. This includes the annual capital cost
 360 (ACC), which is a reflection of mainly the equipment cost and initial solvent circulation cost, as well as
 361 the operating cost, which include variable operating cost (VOC) and fixed operating cost (FOC). The
 362 capital cost of the hybrid CO₂ removal process is higher than the MEA based process by 2.48%. This
 363 is due to the increase in initial solvent circulation rate and high cost of [bpy][BF₄]. It was also observed
 364 that steam cost mainly governs the process operating cost. From the study, the steam cost in the
 365 [bpy][BF₄]-MEA process was reduced by 15.55% compared with the MEA based process. Despite the
 366 increased solvent make-up cost for the [bpy][BF₄]-MEA based process, it was observed that the solvent
 367 make-up cost accounts for small percentage (0.18% and 0.67%) of the total cost of CO₂ removed for
 368 both process. The low steam cost is reflected on the reduced total cost of CO₂ removed in the [bpy][BF₄]-
 369 MEA based process (£19.98/tonne CO₂) compared with the MEA based process (£21.58/tonne CO₂).

370 This showed an energy saving cost of £1.6/tonne CO₂ for [bpy][BF₄]-MEA based process. Based on the
 371 model result, 85,021 tonnes of CO₂ is capture annually. This implies that a savings of £136,033.06 is
 372 attained annually by adopting [bpy][BF₄]-MEA solvent, indicating that the hybrid solvent-based process
 373 is a cost-saving system. See Table 9 for details on the cost of CO₂ removed.

374

375
376

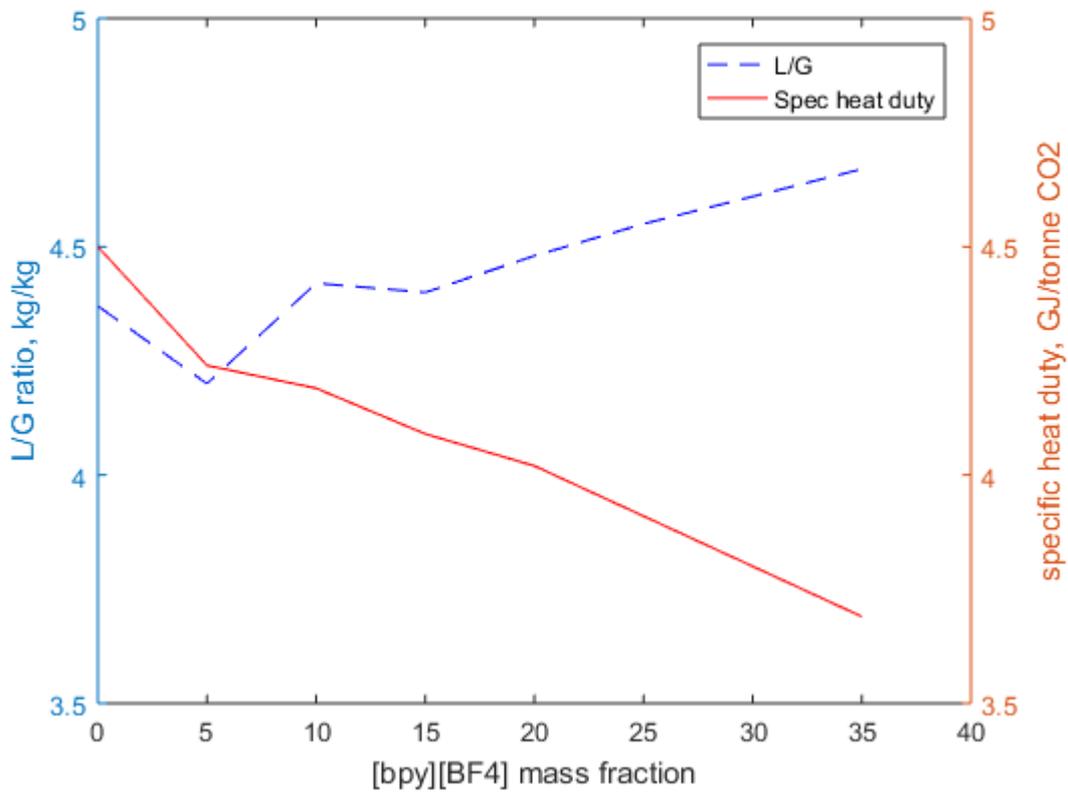
Table 9 Breakdown of the Cost of CO₂ removed for (1) MEA-based process and (2) [bpy][BF₄]-MEA based process

Cost	MEA –based process (£/CO₂ removed)	[bpy][BF₄]-MEA based process (£/CO₂ removed)
ACC	4.15	4.25
VOC steam	7.33	6.19
VOC water	0.67	0.45
VOC electricity	1.91	1.80
Make -up Solvent	0.04	0.13
VOC Miscellaneous	0.20	0.17
FOC	6.37	6.15
Distribution & market	0.08	0.07
R&D cost	0.83	0.75
Total	21.58	19.98

377 **6. Effect of [bpy][BF₄] Concentration**

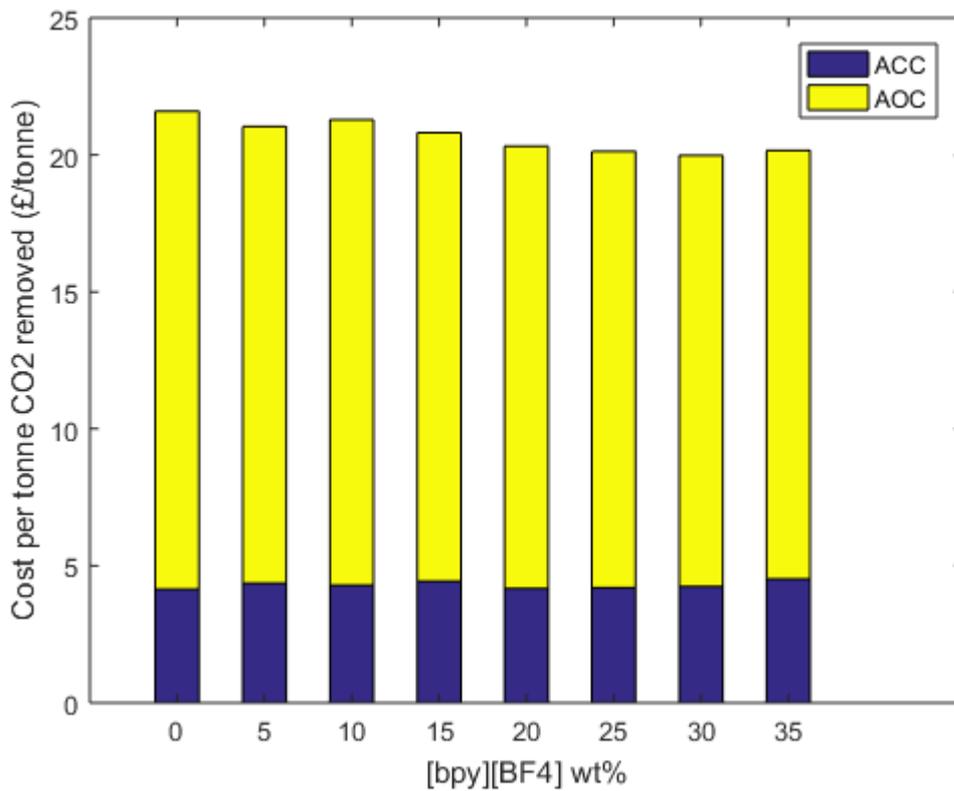
378 **Fig. 11** shows a plot on the effect of [bpy][BF₄] Concentration on the L/G ratio of the absorber and
379 reboiler heat duty. The L/G ratio and specific heat duty reflects the solvent circulation rate and the
380 reboiler steam rate required to meet CO₂ removal specifications. The concentration of [bpy][BF₄] in the
381 hybrid solvent was varied 0wt% to 35wt%. 0wt% of [bpy][BF₄] represents the MEA based process. It
382 was observed that an introduction of a small concentration (5wt%) of [bpy][BF₄] slightly reduces the L/G
383 ratio but a further [bpy][BF₄] concentration increase resulted to relatively steady rise in the L/G ratio.
384 Also, the specific reboiler heat duty reduces as the concentration of [bpy][BF₄] is increased. This
385 indicates that less amount of steam, which basically governs the CO₂ removal cost, is required in the
386 reboiler to meet the CO₂ removal specification with increasing [bpy][BF₄] concentration . This is
387 attributed to decreasing heat capacity of the hybrid solvent as with the presence of [bpy][BF₄] in hybrid
388 solvent.

389 The plot in **Fig. 12** shows the cost of CO₂ removed (as annual capital (ACC) and annual operating cost
390 (AOC)) as a function of the concentration of [bpy][BF₄]. This is to investigate the concentration of
391 [bpy][BF₄] required in the hybrid solvent to achieve the minimum cost of CO₂ removed. **From Fig. 12,**
392 The minimum cost of CO₂ removed (£19.98/tonne CO₂) was attained at 30wt% of [bpy][BF₄]. This is
393 due to the reduced annual operating cost despite the increase in annual capital cost. It can be seen
394 from **Fig. 12** that after 30wt% of [bpy][BF₄], the cost of CO₂ removed increases. This implies that the
395 significance of capital cost to the cost of CO₂ removed increases because of the initial solvent cost
396 increased despite the reduced operating cost.



397

398 Fig. 11 Effect of [bpy][BF₄] mass fraction on L/G (kg/kg) (dashed line) and Specific heat duty
 399 (GJ/tonne CO₂) (straight line) in the [bpy][BF₄]-MEA based process.



400

401 Fig. 12 Effect of [bpy][BF₄] mass percentage on the Cost of CO₂ removed

402 7. Conclusion

403 Application of IL-MEA process for CO₂ capture from power plant flue gases has been [11]. Similar
404 investigation has not been performed for CO₂ removal process in natural gas cleaning in operations.

405 **This study aims to fill the gap by providing a comparative study of conventional MEA and IL-MEA based**
406 **process for natural gas sweetening through modelling and simulation. This study assesses the process**
407 **and energy performance of the hybrid (IL-MEA) solvent, which can replace the conventional amine as**
408 **the future solvent.**

409 The physiochemical properties of IL ([bpy][BF₄]) used in this study were estimated using Aspen Plus®.
410 The results were shown to agree well with the experimental data from literature. The [bpy][BF₄]-MEA
411 based process with lean solvent composition of 30wt% MEA, 30wt% [bpy][BF₄] and 40.0wt% H₂O
412 showed an energy savings of 15% in the reboiler duty and a reduction of 7.44% in the cost of CO₂
413 avoidance compared to the MEA (30wt%) based process. Despite the reduced solvent circulation rate
414 in the MEA based process and high cost of [bpy][BF₄], the hybrid solvent-based process proved to be
415 more cost efficient. This is due to the reduced operating cost of the [bpy][BF₄]-MEA based process as
416 result of the low utilities (majorly steam) cost. Further analysis on the effect of [bpy][BF₄] concentration
417 on the process performance and cost of CO₂ removed was carried out. An increase in the concentration
418 of [bpy][BF₄] resulted in a rise in L/G ratio (solvent circulation rate) and a reduction in the overall energy
419 consumption. Also, the cost of CO₂ removed is reduced with increasing [bpy][BF₄] concentration. From
420 the economic analysis, the 30wt% concentration of [bpy][BF₄] in the [bpy][BF₄]-MEA based process
421 achieved the minimal cost of CO₂ removed. **Thus, [bpy][BF₄]-MEA based solvent was able to achieve**
422 **an energy and cost-efficient capture process.**

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