DBU-glycerol solution: a CO2 absorbent with high desorption ratio and low regeneration energy

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10   **Abstract**

11   1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU)-glycerol solution is employed as a promising CO_2

12   absorbent. The regeneration of the CO_2-loaded solution is of vital importance for its

13   commercialization. It was investigated and compared with 30 wt.% monoethanolamine (MEA).

14   Variables affecting the absorption and desorption processes were studied, including the solvent

15   composition, reaction temperature and agitation. It shows that the absorption capacity for DBU-

16   glycerol is comparable with 30 wt.% MEA, and the desorption ratio for CO_2-loaded DBU-glycerol

17   mixture can reach as high as 95 % in 60 min, 363 K at the 3:1 molar ratio of DBU to glycerol,

18   while it is only 68 % even after 165 min for CO_2-saturated 30 wt.% MEA. DBU-glycerol solution

19   has higher cycling CO_2 loading than 30 wt.% MEA. Its cyclic capacity could keep above 90 %

20   after 10 cycles of absorption-desorption experiments. The desorption reaction is irreversible at the

21   initial stage and the reaction rate is expected as a first-order reaction from 349 K to 377 K, and the

22   apparent activation energy is 68.94 kJ/mol. Moreover, the heat duty of the reboiler during

23   regeneration is estimated to be reduced by about 27 % when compared with 30 wt.% MEA.

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25   **TOC**

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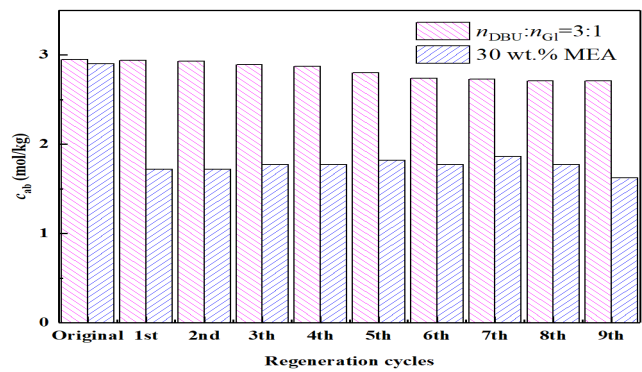
27   **1.   Introduction**

28   Huge amount of CO_2 emission is believed to be one of the major reasons of the global warming.

29   Carbon capture and storage (CCS) is currently the most promising way to reduce the CO_2

30   emission since it is compatible with the existing emission system [1-5]. Aqueous alkanolamines

31   such as MEA have been used in the post-combustion CO_2 capture (PCC)[6]. Considering the

32   effects of corrosion, degradation, and energy consumption during regeneration[7-11], 30 wt.% MEA

33   is usually adopted as a benchmark in the commercialization.

34   The energy required for solvent regeneration accounts for 70-80% of the total energy

35   consumption[7, 12]. Development of new solvents with low regeneration energy demand has

36   attracted great attention of both the academy and industry. During the regeneration process, there

37   are mainly three parts of energy consumption, including the reaction heat of desorption, the

38   latent heat of vaporization, and the sensible heat. In conventional aqueous amine solution, large

39   energy is consumed on the vaporization of water, meanwhile, the high specific heat of water also

40   increases the sensible heat. If water-lean or non-aqueous solvents with high boiling points and

41   low specific heat are used, it may reduce the energy consumption during regeneration. And many

42   researchers have reported this kind of solvents in CO_2 capture[13-15]. Barzagli et al.[13] studied

43   aminomethylpropanol(AMP) and some AMP-alkanolamine blends in non-aqueous solvents

44   which were a mixture of ethylene glycol and 1-propanol or single diethylene glycol monomethyl

45   ether. Both batch and continuous experiments were studied. And they found the CO_2 removal

46   efficiency can reach 87-95%. Tan et al.[14] investigated the solubility of CO_2 in MEA-triethylene

47   glycol(TEG) solution. Their mathematical model showed that the absorption and desorption can

48   be realized at temperature lower than 353.15K and it may decrease the energy consumption.

49   Bougie et al.[15] studied the non-aqueous MEA solutions with three kinds of solvents: diethylene

50   glycol monoethyl ether(DEGMEE), N-methylformamide(NMF), ethylene glycol/1-propanol

51   mixture. And DEGMEE solutions showed lower energy consumption than 30 wt.% MEA

52   solution during regeneration. Recently, research showed that DBU-alcohol solution has a CO_2

53   capacity as high as 19 wt.% [16] which is much higher than that of 30 wt.% aqueous MEA ($\leq$7

54   wt.%) [16-17]. CO_2 could be released from the solution of the resultant ionic compounds (amidium

55   alkylcarbonates[18]) upon heating to a certain temperature, and the DBU-alcohol solution was

56   regenerated accordingly. It is also found that this kind of absorbents has significantly lower

57   specific heat capacity, which is about half of water[19]. This could lead to less energy consumption

58   due to reducing the sensible heat in the regeneration process[20].

59   The high boiling point of DBU (260 °C) decreases the evaporation of solvent. Glycerol, with a

60   boiling point of 290 °C, can be readily available from the biodiesel production. Compared with 1-

61   propanol and 1-hexanol[13, 19], higher boiling points of DBU and glycerol than 1-propanol (97℃)

62   and 1-hexanol(157℃) are preferred due to less evaporation of solvent. The physicochemical

63   properties such as the density, viscosity, conductivity, surface tension as well as the CO_2

64   solubility of the resultant DBU-glycerol solution have been well investigated[20-23]. This work

65   focused on the performance of DBU-glycerol solvent in CO_2 absorption and desorption

66   processes. The effect of solvent composition, operation temperature and the cyclic absorption-

67   desorption performance of DBU-glycerol solvent were systemically investigated. The kinetics of

68   the regeneration was studied. Meanwhile, the energy consumption for solvent regeneration was

69   estimated accordingly and compared with that of 30 wt.% MEA.

70   **2.   Materials and methods**

71   2.1 Materials and instruments

72   MEA (>98.0 %) and glycerol (>99.0 %) were purchased from Chengdu Chron Chemical Reagent

73   Co., Ltd., China. DBU (>99 %) was purchased from Shanghai Beihe Chemical Industry, China.

74   The gases (CO_2, >99 % and N_2, >99.99 %) were supplied by Chengdu Dongfeng Gas Plant. All

75   reagents were used directly without further purification.

76   Mass flow controller (MFC, D08-2F, Beijing Sevenstar Electronics Co. Ltd., China) and a CO_2

77   infrared analyzer (FN316B, Shanxi FeiEnTe Instrument Technology Co. Ltd., China) were used

78   in the absorption and desorption experiments. A differential scanning calorimeter (DSC 214

79   Polyma, Netzsch, Germany) and a simultaneous thermal analyzer (STA 449F3 Jupiter, Netzsch,

80   Germany) were used to measure the heat capacity and the reaction heat for absorption process.

81   2.2 The absorption and desorption of CO_2

82   **Fig. 1a** shows the schematic diagram of the absorption experiment. The absorbent (30.00g) was

83   firstly put in the three-neck flask, which was settled at 313 K in an oil bath. CO_2 with a flow rate

84   of 200 ml/min controlled by a mass flow controller was bubbled to the solvent. As soon as CO_2

85   was bubbled to the solvent, start the mechanical stirring to ensure the full contact between gas

86   and liquid.

87   When DBU-glycerol solution was used as an absorbent, considering the high boiling points of

88   DBU and glycerol, CO_2 absorbed by the solvent can be calculated by the mass difference before

89   and after the absorption[21], which is calculated as follows:

$$m_{CO_2} = m_t - m_0 \tag{1}$$

91   The error of the balance is 0.01g. In addition, the CO_2 loading c_{ab} (mol/kg) in the solvent can be

92   calculated as follows:

$$c_{ab} = \frac{m_{CO_2} \times 10^3}{M_{CO_2} \times m_{absorbent}} \tag{2}$$

94   Where, m_0 and m_t are the total mass of the absorbent and the flask before and after the absorption

95   (g), respectively. m_{CO2} and $m_{absorbent}$ are the mass of CO_2 and absorbent (g), respectively. M_{CO2} is

96   the molecular weight of CO_2 (44 g/mol). Meanwhile, the conversion of –OH group in glycerol

97   can be calculated as follows:

$$x_{-OH} = \frac{c_{ab}}{3 \times c_{glycerol}} \times 100\% \tag{3}$$

99   Here $c_{glycerol}$ is the mole concentration of glycerol (mol/kg) in the absorbent, which can be

100   calculated as

$$c_{glycerol} = \frac{m_{glycerol}}{92 \times (m_{DBU} + m_{glycerol})} \times 1000 \tag{4}$$

102   m_{DBU} and $m_{glycerol}$ are the masses of DBU and glycerol in the initial absorbent.

103   The relative error of the method is less than 2%.

104   When 30 wt.% MEA was used as an absorbent, c_{ab} was determined by the $BaCO_3$ precipitation

105   titration method[24], with an error of ±0.05 mol/kg.

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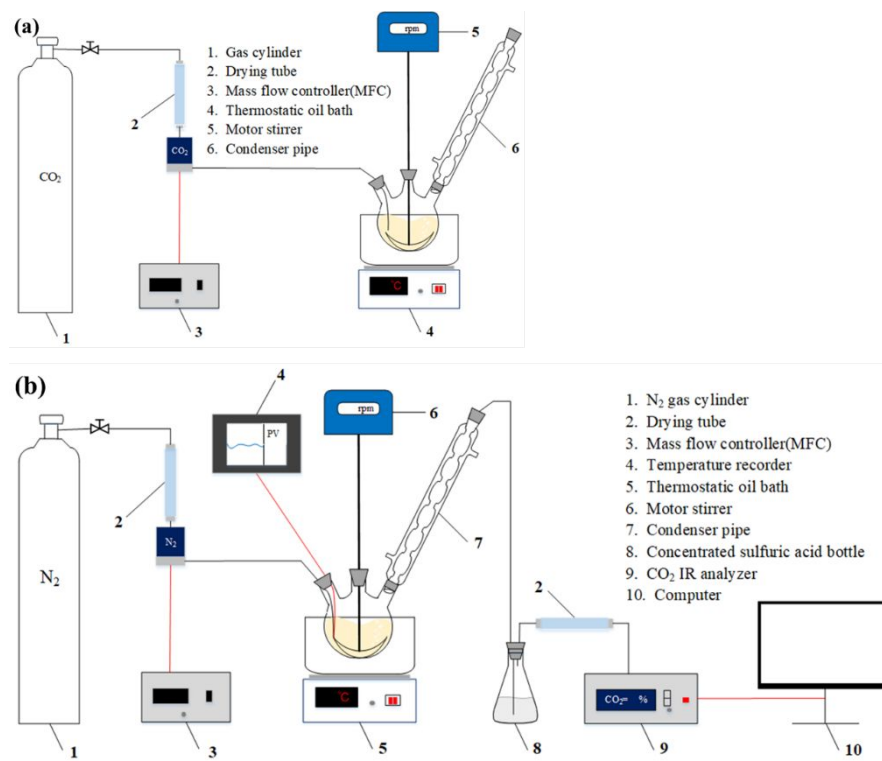
107   **Figure 1.** The schematic diagram of the absorption (a) and desorption (b) experiment

108   **Fig. 1b** shows the schematic diagram of the regeneration experiment. After the absorption, the

109   CO_2-loaded solution in the flask was immersed in the oil bath to maintain it at the required

110   temperature. N_2 was used to blow out the generated CO_2, and the outlet gas was successively

111   passed through the condenser pipe, concentrated sulfuric acid bottle, drying tube, and a CO_2

112   infrared ray analyzer.

113   The desorption rate of CO_2, v_{CO2} (mol·kg^{-1}·min^{-1}), can be calculated by the flow rate of N_2, as

114   shown in the following formula.

115
$$v_{CO_2} = \frac{1000 \times q_{N_2} \times \frac{y}{(1\text{-}y)}}{22.4 \times m_{absorbent}}$$
(5)

116　　Where, y is the CO_2 concentration in the outlet gas (%), and q_{N2} is the volume flow rate of N_2

117　　(ml/min) measured by MFC.

118　　The conversion, which is also the desorption ratio, x (%) is used to describe the extent of the

119　　desorption, and calculated as follows:

120
$$x = \frac{c_{A0} - c_A}{c_{A0}} \times 100\%$$
(6)

121　　Where, c_{A0} is equal to the CO_2 loading at the end of absorption, c_A is the CO_2 loading which

122　　changes with time, it can be calculated by the time integration of the CO_2 desorption rate. The

123　　error of the experimental data is less than 10 %.

124　　**3.　Results and discussion**

125　　3.1　Effect of the molar ratio of DBU to glycerol on CO_2 capacity of DBU-glycerol solvent

126　　The proposed reaction scheme of DBU- glycerol with CO_2 can be seen in **Fig. 2**. Theoretically,

127　　one CO_2 molecule can react with one –OH group and one DBU molecule. As there are three –

128　　OH groups in one glycerol molecule, the absorption performance will be affected by the

129　　composition of DBU-glycerol solution.
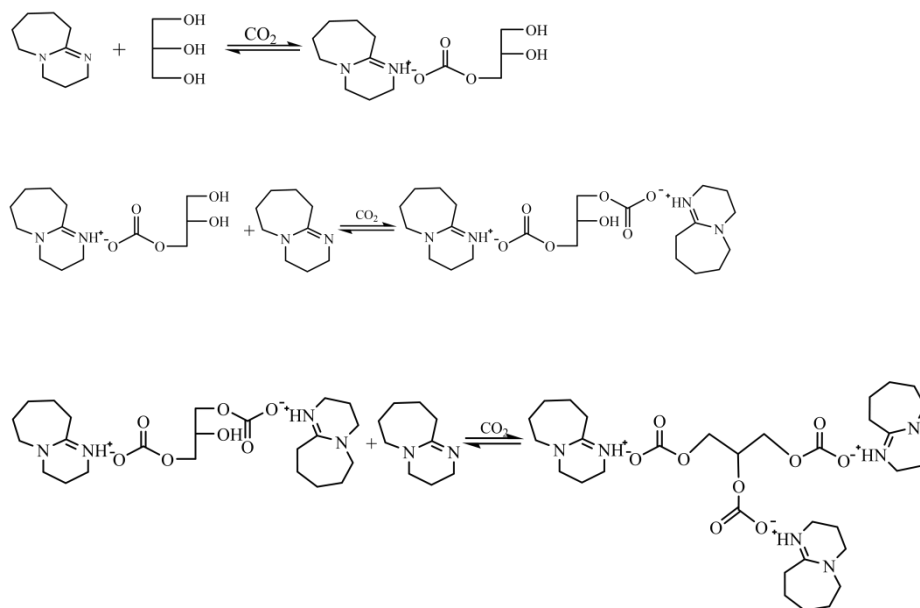
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131   **Figure 2.** The proposed reaction scheme of DBU- glycerol with CO_2[21, 25].

132   **Fig. 3** shows the absorption loadings of CO_2 in DBU-glycerol solution with different initial

133   molar ratios at different time and that of 30 wt.% MEA is compared. From **Fig. 3**, it shows that

134   the absorption rates are quite different for DBU-glycerol solution and 30 wt.% MEA. Among

135   them, 30 wt.% MEA has the highest absorption rate in the first 30 min. The CO_2 loading

136   increases to the highest in 30 min and keeps almost the same from 30 min to 120 min. For DBU-

137   glycerol solution, according to Fu's result[26], the primary –OH groups of glycerol have the

138   priority to participate in the reaction, and it is very hard for the secondary –OH group to react.

139   Since there are two primary –OH groups in glycerol, only one will react at first due to the steric

140   hindrance effect as in **Fig. 2**. When the molar ratios are 3:1, 2:1, 1:1 and 1:2 for DBU and

141   glycerol, the concentration of the primary –OH groups which have the priority to react in the

142   absorption are 1.82 mol/kg, 2.52 mol/kg, 4.09 mol/kg and 5.94 mol/kg. Meanwhile, the DBU

143　　　concentration are 5.47 mol/kg, 5.04 mol/kg, 4.09 mol/kg and 2.97 mol/kg, respectively.

144　　　Generally, higher concentrations of the primary –OH groups and DBU are beneficial to higher

145　　　reaction rate. As a result, the initial reaction rates for $n_{DBU}:n_{Gl}$=1:1 and $n_{DBU}:n_{Gl}$=1:2 are higher

146　　　than those of $n_{DBU}:n_{Gl}$=2:1 and $n_{DBU}:n_{Gl}$=3:1. After 120 min, the CO_2 loadings were 2.93 mol/kg,

147　　　3.13 mol/kg, 3.61 mol/kg and 3.02 mol/kg for $n_{DBU}:n_{Gl}$=3:1, $n_{DBU}:n_{Gl}$=2:1, $n_{DBU}:n_{Gl}$=1:1 and

148　　　$n_{DBU}:n_{Gl}$=1:2, respectively. Correspondingly, the converted –OH groups in glycerol were 54 %,

149　　　41 % , 29 % and 17 % for DBU and glycerol with the molar ratio of 3:1, 2:1, 1:1 and 1:2,

150　　　respectively. It means that the second reaction in **Fig. 2** takes place when the ratios are 3:1 and

151　　　2:1. For DBU and glycerol solution with the molar ratio of 1:1 and 1:2, only the first reaction in

152　　　**Fig. 2** takes place. However the CO_2 loadings are comparable with that of 30 wt.% MEA after

153　　　120 min.

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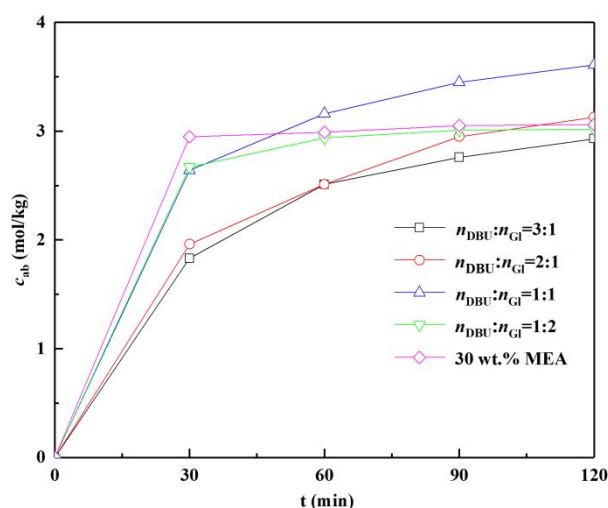
155 **Figure 3.** The absorption loading of DBU-glycerol with different molar ratios and 30 wt.%

156 MEA.(CO_2: 200 ml/min, 313 K, 500 rpm.)

157 3.2 The desorption performance of DBU-glycerol-CO_2 solution

158 3.2.1   Effect of the molar ratio of DBU to glycerol

159 To investigate the effect of the molar ratio of DBU to glycerol on CO_2 desorption performance,

160 CO_2-rich solutions with the same initial CO_2 loadings (**Fig. 4**) were studied. Considering the high

161 viscosity of DBU-glycerol solutions[23], the CO_2 loadings were kept at 1.60 mol/kg (~7 wt.%) in

162 DBU-glycerol-CO_2 solutions, which is usually the loading of 30 wt.% MEA in commercialized

163 process[16-17]. At this CO_2-loading, DBU can only react with one –OH group of glycerol in the

164 solution[26]. To remove the regenerated CO_2 as soon as possible, N_2 was bubbled in the solution.

165 **Fig. 4** shows the effect of composition on desorption of the CO_2-rich solution. Obviously, both

166 the desorption rate and the desorption ratio are affected by the composition of the solution.

167 Increasing the molar ratio of DBU and glycerol from 1:2 to 3:1 leads to a significant increase in

168 the initial desorption rate and the final desorption ratio. It is probably due to the difference in

169 polarity of the solutions. For DBU-glycerol solutions with molar ratios of 3:1, 2:1, 1:1 and 1:2,

170 when the CO_2 loading is 1.60 mol/kg, after the absorption, the unreacted DBU contents in the

171 mixture are 55 wt.%, 49 wt.%, 35 wt.% and 19 wt.%, respectively. Correspondingly, the

172 unreacted glycerol contents are 2 wt.%, 8 wt.%, 21 wt.% and 37 wt.%. In DBU-alcohol-CO_2

173 system, the existence of non-polar solvent can promote the desorption of CO_2[27]. Here, the

174   unreacted DBU is non-polar while glycerol is polar. So higher DBU content is beneficial to

175   desorption. For DBU-glycerol solution with a molar ratio of 3:1, the desorption ratio can reach as

176   high as 95 % in 60 min. But for the solution with a molar ratio of 1:2, the desorption ratio is only

177   52 % even after 230 min. In addition, for 30 wt.% MEA solution, the desorption rate and the

178   desorption ratio are higher for higher CO_2 loading. But whether the CO_2 loading is 3.04 mol/kg

179   (saturated) or 1.60 mol/kg, the initial desorption rate is lower than DBU-glycerol solution with a

180   molar ratio of 3:1 when the CO_2 loading is 1.60 mol/kg. Also, for 30 wt.% MEA, the desorption

181   ratio is only 68 % after 165 min with a CO_2 loading of 3.04 mol/kg and only 60 % after 180 min

182   with a CO_2 loading of 1.60 mol/kg, which are much lower than that of CO_2-loaded DBU-

183   glycerol solution with a molar ratio of 3:1 when the CO_2 loading is 1.60 mol/kg. Compared with

184   the ionic compound DBU/glycerol/CO_2(DGC), which begins to decompose at about 60 ℃[25],

185   carbamates are stabler. Their regenerations are more difficult at lower temperatures, resulting in

186   lower desorption ratios. Considering the desorption rate and the desorption ratio, DBU-glycerol

187   solution with a molar ratio of 3:1 is optimal for further study. In addition, the desorption ratio for

188   DBU-glycerol solution with a molar ratio of 3:1 is much higher compared with other non-

189   aqueous solutions such as AMP, and AMP-alkanolamine blends in the solvents including the

190   mixture of ethylene glycol and 1-propanol or single diethylene glycol monomethyl ether, most of

191   the desorption ratios were below 60 % in 60 min at 90 ℃[13].

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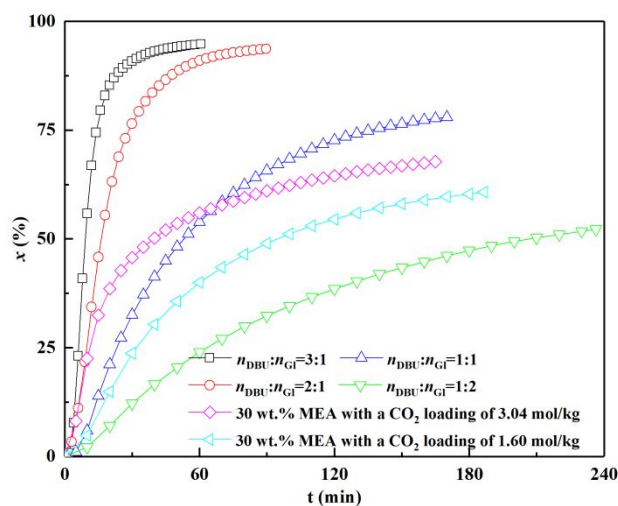
Figure 4. Desorption ratio of DBU-glycerol with different molar ratios.(Initial CO_2 loading for

DBU-glycerol solution: 1.60 mol/kg, N_2:200 ml/min, 363 K, 500 rpm.)

3.2.2   Effect of agitation

The desorption process consists of the decomposition of DGC and the release of CO_2 from the

liquid phase to the gas phase. Stirring can make the mixture uniform, which is beneficial to heat

and mass transfer. The effect of agitation was investigated in **Fig. 5**. N_2 was blowing on the

surface of the liquid.

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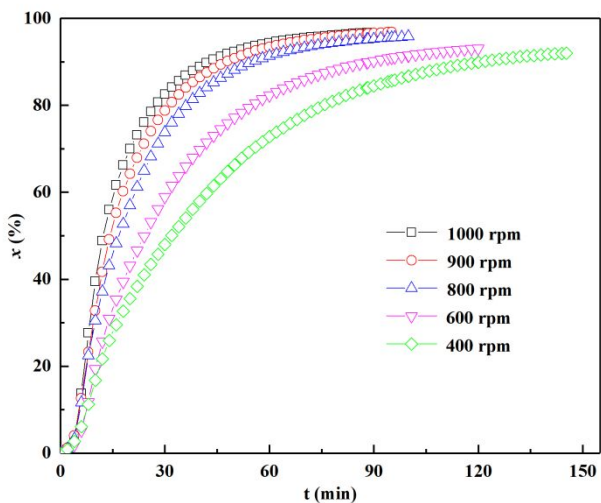
Figure 5. The effect of agitation on the desorption.(n_{DBU}: n_{Gl} =3:1, initial CO_2 loading: 1.60

mol/kg, N_2:200 ml/min, 363 K.)

From **Fig. 5**, the agitation has obvious effect on desorption ratio from 400 rpm to 800 rpm. For

the same time, the desorption ratio is higher at higher stirring speed. The desorption ratio can

reach 73 %, 82 % and 91 % in 60 min for 400 rpm, 600 rpm and 800 rpm, respectively. But

continue increasing the stirring speed from 800 rpm to 1000 rpm, the desorption ratio increased

only from 91 % to 94 %. The agitation promotes the mixing of the solution, and makes the

solution uniform in both temperature and composition. However, when the stirring speed

increased to 900 rpm, further increase of stirring speed has little effect on the desorption. So 900

rpm is considered as an optimal stirring speed.

3.3 Kinetics of the desorption for DBU-glycerol-CO_2 solution

212   Temperature is an important factor affecting the CO_2 desorption. **Fig. 6** shows both the

213   desorption rate and ratio of DBU-glycerol-CO_2 solution at different temperatures. Obviously,

214   higher temperature is beneficial to desorption. From 349 K to 377 K, the maximum desorption

215   rate increases about 7.6 times. Meanwhile, in 20 min, the desorption ratio reaches as high as 88

216   % at 377 K while it is only 26 % at 349 K. And the desorption ratio is 99 % which is almost

217   complete in 60 min at 377 K, and the desorption ratio is only 90 % even after 150 min at 349 K.

218   Compared with 30 wt.% MEA which usually requires about 120℃ to accomplish the desorption

219   in the industry, DBU-glycerol with a molar ratio of 3:1 needs lower temperature for regeneration.

220   Therefore, it is much helpful to decrease the energy consumption during regeneration process.
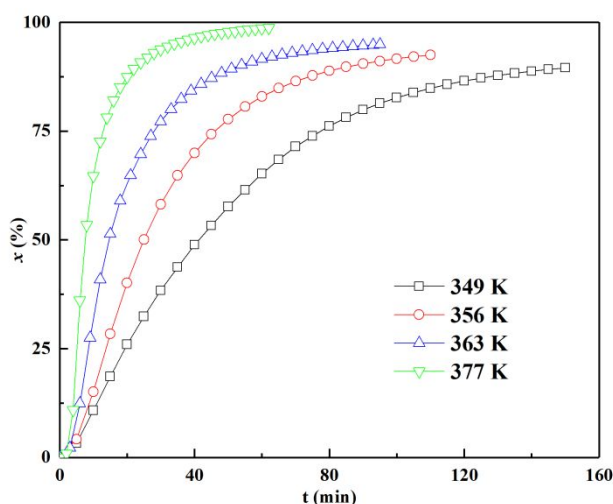

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222   **Figure 6.** Desorption ratio performance of the CO_2-rich absorbents at different temperatures.

223   (n_{DBU}: n_{Gl} =3:1, initial CO_2 loading: 1.60 mol/kg, N_2:200 ml/min, 900 rpm.)

224   According to **Fig. 6**, the desorption of CO_2 in DBU-glycerol-CO_2 solution can be considered as

225   an irreversible reaction when the desorption ratio is low. To investigate the kinetics of

226   desorption, the following assumptions are proposed at first.

227   1. The desorption process is irreversible at the initial stage.

228   2. The desorption rate is proportional to the concentration of DGC.

229   As a result, the desorption reaction rate can be written as follows:

230
$$r = -\frac{dc_A}{dt} = kc_A \tag{5}$$

231
$$-\frac{dc_A}{c_A} = kdt \tag{6}$$

232
$$-\ln(1-x) = kt \tag{7}$$

233   Where, k is the rate coefficient, c_A is the concentration of DGC, t is the reaction time, and x is

234   the conversion of DGC.

235   According to **Fig. 6**, the relationship between -ln(1-x) and t can be obtained when x is less than

236   80 %, which is shown in **Fig. 7**. It can be seen that -ln(1-x) has a good linear relationship with t,

237   and the reaction rate constant increases gradually with the increase of temperature. The

238   desorption rate of CO_2 can be described by a first-order equation under the experimental

239   conditions. When x is higher than 80 %, the linear relationship between -ln(1-x) and t disappears.
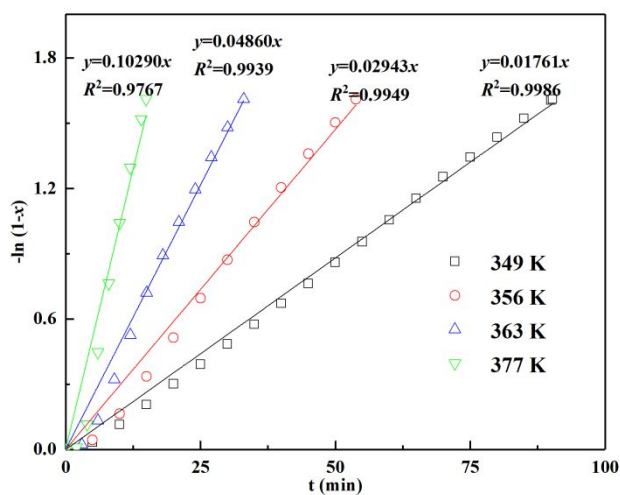
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241   **Figure 7.** Relationship between -ln(1-x) and t.

242   According to Arrhenius law,

243
$$\ln k = \ln k_0 - \frac{E_a}{RT}$$
(8)

244   Where, k_0 is the pre-exponential factor (min^{-1}), E_a is the activation energy (J·mol^{-1}) of CO_2

245   desorption, and R is the ideal gas constant (8.314 J·mol^{-1}·K^{-1}).

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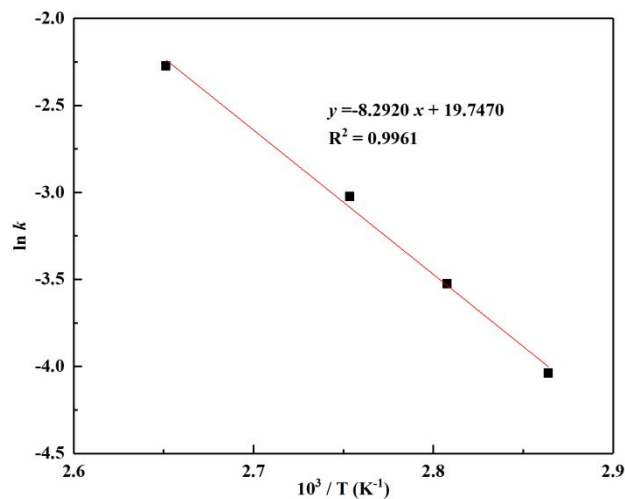
247   **Figure 8.** Arrhenius plots for the desorption of DBU-glycerol-CO_2.

248   The relationship between k and T^{-1} is shown in **Fig. 8**. E_a value of 68.94 kJ/mol and k_0 value of

249   7.44×10^8 min^{-1} are regressed. Therefore, the Arrhenius form of CO_2 desorption from DBU-

250   glycerol-CO_2 is：

251    $$k = 7.44 \times 10^8 e^{\frac{-68940}{RT}} \text{ (min}^{-1}\text{)} \tag{9}$$

252   3.4 Absorption-desorption circulating

253   Ideal absorbents should have good regeneration stability. To investigate the absorption-

254   desorption circulating performance of DBU-glycerol solution, 10 cycles of absorption-desorption

255   experiments for both DBU-glycerol solution and 30 wt.% MEA were investigated(**Fig. 9**). The

256   original CO_2 loading of the two systems is almost the same (2.98 mol/kg vs 2.90 mol/kg), but the

257   cyclic capacity is quite different. After 10 cycles of absorption-desorption, the cyclic capacity is

258   more than 90 % of the initial loading for DBU-glycerol. For 30 wt.% MEA, the CO_2 loading is

259   about 2.90 mol/kg for the first absorption, the average cyclic capacity is 1.72 ± 0.05 mol/kg,

260   which is only about 60 % of the initial loading. It is much lower than that of DBU-glycerol

261   solution.

262
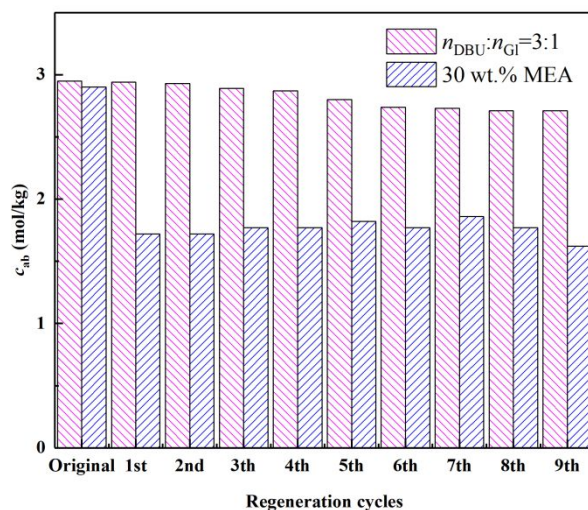
263   **Figure 9.** Cyclic capacity of CO_2 for DBU-glycerol with a molar ratio of 3:1 and 30 wt.%

264   MEA.(absorption: 313 K, CO_2:200 ml/min; 120 min, desorption: 363 K, N_2:200 ml/min.)

265   3.5 Estimation of regeneration energy demand for DBU-glycerol and 30 wt.% MEA solution

266   In the absorption of CO_2, the high regeneration energy cost is the bottleneck for an absorbent

267   which comes mainly from the reboiler heat duty in the stripping tower[28]. Here, the reboiler heat

268   duty is estimated for the DBU-glycerol (molar ratio 3:1) solution with a CO_2 loading of 1.60

269   mol/kg (~7 wt.%) to estimate the regeneration energy consumption for DBU-glycerol-CO_2

270   solution, and the result is compared with that of CO_2-saturated 30 wt.% MEA aqueous solution

271   with a CO_2 loading of 2.90 mol/kg under the same assumed desorption conditions. The

272   regeneration energy (Q) consists of three parts: the reaction heat of desorption (Q_r), the latent

273   heat of vaporization (Q_v), and the sensible heat (Q_s)[24, 29-32]. The calculation formulas are as

274   follows[24]:

$$Q_s = \frac{C_p m_L \Delta T}{m_{CO_2}} = \frac{C_p \Delta T}{c_{ab} x M_{CO_2}} \tag{10}$$

$$Q_r = \frac{n_{CO_2} \Delta H}{m_{CO_2}} = \frac{\Delta H}{M_{CO_2}} \tag{11}$$

$$Q_v = \frac{n_w \Delta H_{H_2O}}{m_{CO_2}} = \frac{n_w \Delta H_{H_2O}}{n_{CO_2} M_{CO_2}} \tag{12}$$

278   where C_p is the constant pressure heat capacity($kJ·kg^{-1}·K^{-1}$), ΔT is the temperature difference

279   between the top and bottom of the desorption tower (K), ΔH is the reaction heat (kJ/mol), and

280   n_w/n_{CO_2} is the molar ratio of water and CO_2 in the top of the tower.

281   Furthermore, as the regeneration conditions greatly affect the energy consumption, to estimate

282   the heat duty, the operating conditions are assumed as follows:

283   1.The absorption is carried out at 313 K, and the CO_2-rich solution are heated to 355 K by an

284   intermediate heat exchanger and sent to the desorption tower with an average temperature of 363

285   K (top:355 K, bottom:371 K), and the desorption pressure is 101.3 kPa;

286   2. The regeneration ratio of DBU-glycerol-CO_2 is 90 %, while for 30 wt.% MEA it is 60 %;

287   3. As the boiling points of DBU, glycerol and MEA are much higher than the desorption

288   temperature, the latent heat of vaporization can be ignored. And the reflux of DBU and glycerol

289   is ignored in DBU-glycerol solution, only water for 30 wt.% MEA is refluxed.

290   4. For 30 wt.% MEA, the reflux ratio (n_w/n_{CO2}) is mainly dependent on the water content in the

291   solution and the regeneration temperature[29]. And the value is equal to p_{H2O}/p_{CO2}. According to

292   Dalton's law of partial pressure and Raoult's law[31],

$$p_{\text{total}} = p_{\text{CO}_2} + p_{\text{H}_2\text{O}} \tag{13}$$

$$p_{\text{H}_2\text{O}} = x_{\text{w}} p_{\text{w}}^{\text{vap}} \tag{14}$$

295   The saturated vapor pressure of water is 51.3 kPa at 355 K on the top of the tower. The mole

296   percent of water is approximately 83 % in CO_2-rich 30 wt.% MEA solution. So, the reflux ratio

297   is 0.73.

298   To calculate the sensible heat (Q_s), C_p is needed to be measured at first. According to the

299   literature, C_p can be obtained from a differential scanning calorimeter[33]. The curves are shown in

300   **Fig. S1(Supporting Information)**. The heat capacities of CO_2-rich DBU-glycerol and 30 wt.%

301   MEA at 363 K were calculated by extrapolation, which are 2.83 and 3.95 kJ·kg^{-1}·K^{-1},

302   respectively. In addition, the reaction heat of desorption is approximately the same as that of

303   absorption, so the absorption heat can be used to represent the desorption heat. The absorption

304   heat is measured by a simultaneous thermal analyzer[34] and the result curve is presented in **Fig.**

305   **S2**. The reaction heat of 30 wt.% MEA is 91.3 kJ/mol[35], which is consistent with the literature

306   value (80~110 kJ/mol)[30, 36-37]. And for DBU-glycerol system it is 84.6 kJ/mol.

307   All the parameters needed to calculate the regeneration energy consumption are listed in **Table 1**

308   and the energy consumption are estimated in **Table 2**. As we can see, although the absorption of

309   CO_2 by DBU-glycerol mixture cannot reduce the reaction heat to a large extent, the sensible and

310   latent heat can be reduced due to the high boiling point and low heat capacity, so reduce the total

311   energy consumption. The regeneration energy consumption of 30 wt.% MEA was calculated to

312   be 3.61 GJ/ton CO_2, corresponding to the generally 3.50-4.30 GJ/ton CO_2[38-41], while it was 2.63

313   GJ /ton CO_2 for DBU-glycerol. So the energy consumption of desorption CO_2 per ton can be

314   reduced by about 27 % compared with 30 wt.% MEA.

315   Although the results are promising, one phenomenon should be noticed that water was not

316   considered in the system. As water is generally contained in the flue gas, it probably accumulates

317   in the system during absorption-desorption process because both DBU and glycerol are

318   hydrophilic, which will possibly affect the absorption and desorption processes further change

319   the final energy consumption. The results (showed in Figures S3 and S4) of 10 wt%

320   (n_{DBU}:n_{Gl}:n_{H2O} =5.90:1.77:1) or 20 wt% (n_{DBU}:n_{Gl}:n_{H2O} =2.95:0.79:1) of glycerol replaced by

321   water show that at the presence of water the desorption ratio will decrease whereas the CO_2

322   absorption capacity is even higher than that of pure DBU-glycerol system. However, both of the

323   CO_2 absorption capacity and desorption ratio are higher than those of 30 wt% MEA. Therefore,

324   considering the lower specific heat of DBU-glycerol than water, the presence of water in DBU-

325   glycerol system is still helpful for the regeneration of CO_2 with lower energy compared with 30

326   wt% MEA[19]. Besides, the optimization for the full process was not included either. To evaluate

327   the energy consumption more accurately, substantial research should be done in the future.

328   **Table 1.** Parameters for estimating energy consumption

	DBU-glycerol(molar ratio, 3:1)	30 wt.% MEA
C_p (kJ/(kg·K))	2.83	3.95
ΔT (K)	16	16
c_{ab} (mol/kg)	1.60	2.90
x (%)	90	60
ΔH (kJ/mol)	84.6	91.3
ΔH_{H2O} (kJ/mol)	-	42.3
n_w/n_{H2O}	-	0.73

329   **Table 2.** Results of energy consumption estimation

	DBU-glycerol(molar ratio, 3:1) (GJ/ton CO_2)	30 wt.% MEA (GJ/ton CO_2)
Q_s	0.71	0.83
Q_r	1.92	2.08
Q_v	0	0.70
Q	2.63	3.61

330   SUPPORTING INFORMATION

331   Figure S1shows the curve of specific heat capacities of absorbents at various temperatures.

332   Figure S2 shows the TG–DSC curves for the absorption of CO_2 in DBU-glycerol mixture at

333   313K.

334   Figure S3 shows the absorption of CO_2 in different solutions.

335   Figure S4 shows the desorption of CO_2 in different solutions with different initial CO_2 loadings.

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