Study on the effect of operating parameters towards CO_2 absorption behavior of choline chloride – Monoethanolamine deep eutectic solvent and its aqueous solutions

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ABSTRACT

In this study, the effect of absorption pressure and temperature towards the CO_2 absorption capacity and rate of choline chloride - monoethanol amine deep eutectic solvent (ChCl-MEA DES) was evaluated. Water mixing into ChCl-MEA DES was also examined as a method to improve CO_2 absorption behavior. Equilibrium experiments were done in a batch reactor and the data was analyzed using response surface methodology (RSM). Results suggested that the dominant mode of CO_2 absorption by ChCl-MEA DES was physical absorption. The maximum capacity of CO_2 absorption obtained in this study was 0.379 mol-CO_2/mol-DES from absorption at (10 bar, 40 °C) using DES with 50 %v water. Water mixing up to 50 %v was found to nearly double the CO_2 absorption capacity of ChCl-MEA DES compared to neat DES. Study into CO_2 absorption rate by ChCl-MEA DES found that it is mainly influenced positively by pressure and water content, while not significantly influenced by temperature. CO_2 absorption rate of ChCl-MEA DES with 50 %v water was found to be on average twice of that of neat DES. It was also found that water content up to 50 %v does not change the mechanism of CO_2 absorption by ChCl-MEA DES.

1. Introduction

Gasification is one of the novel thermochemical processes to convert solid fuel to gas products known as syngas. This gas mainly consists of H_2, CO, CO_2, and CH_4. Syngas has a wide range of applications, from energy generation to chemical feedstock. When syngas is used as chemical feedstock, CO_2 removal usually is necessary to achieve desirable syngas composition. This is especially important since syngas that has gone through water gas shift reactor or syngas from advanced processes such as supercritical water gasification could contain up to 50 % volume of CO_2 [1]. The removal of this excess CO_2 would allow for the syngas to be used for more advanced applications with stricter gas composition requirements; such as for ethanol or dimethyl ether production, and hydrogen fuel [2,3]. The separated CO_2 could also be utilized for various purposes, such as to enhance the performance of the gasification process itself [4].

The most widely used method for CO_2 removal from gas phase is absorption with amine solution [5]. However, this method still faces inherent problem such as huge amine loss and extensive energy consumption due to the solvent regeneration by heating [6–9]. Other processes utilizing physical absorption, such as Rectisol and Selexol, are also available. The problem with these methods is how the absorption process must be done at low temperature, around -60 °C, to ensure the stability and efficiency of the absorbents [10]. These sorts of requirement demand complex equipment and significant consumption of energy. Therefore, the development of absorbents that could be used in more moderate operating conditions and could be regenerated effectively could be a solution for applying CO_2 removal in efficient manner.

In the last decade, a mixture with special characteristic is gaining attention as CO_2 removal solvent by absorption. In the publication in 2006, Abbott called this group of mixture "Deep Eutectic Solvent" (DES) [11]. The name is based on its special characteristic, in which its melting temperature of the mixture is lower than that of its constituents. DES absorbs CO_2 by physical means, which could lead to less energy

intensive regeneration and less absorbent loss compared to chemical absorbents. Another inherent benefit is that DES is stable at room temperature, this eliminates the need to chill the absorbent to very low temperature such as for other physical absorbents [12].

A few types of DES, including those prepared from choline-like materials, have also been proven to work well for desulfurization [13,14]. With H_2S being one of the most common contaminants in syngas [15], DES could offer another potential benefit for the application of acid gas removal from syngas. Another often-touted advantage of DES is its cheap and simple preparation. It is often done by mixing the solid or liquid pure components in a vial, heating them to around 70 – 80 °C while stirred for a few hours. DES would form usually in the form of a colorless viscous liquid, although some might have a certain colored hue [16–18]. Unlike ionic liquids, DES preparation is a mixture process and hence does not necessitate further purification of DES before use.

Various types of DES have been examined for CO_2 removal application. DES such as choline chloride (ChCl) + urea, ChCl + glycerol, and ChCl + ethylene glycol has been exhibiting potential as CO_2 absorption solvent [19–25]. In the last two years, a few studies have shown that amine-based ChCl DES have high CO_2 solubility, even higher than conventional aqueous amine solvent [17,24]. With a study by Adeyemi et. al. [17] finding that among all the ChCl + amine DES, ChCl + monoethanolamine deep eutectic solvent (ChCl-MEA DES) had the highest CO_2 solubility [26].

Despite the potentials, one major challenge to DES application in industrial scale processes is its high viscosity. ChCl-MEA DES at room temperature has a viscosity value of 49.5 cP, much higher than amine solvents [26]. Taking a cue from amine application [5], one proposed solution to this issue is by mixing water into DES to form an aqueous solution of the absorbent. A few studies have suggested that DES is able to remain stable even in the presence of water [27–29]. Hammond et al. found that ChCl – malic acid (MA) DES was able to retain its stable structure in a mixture of up to 50 %v water [30,31]. A molecular simulation study by Zhekenov et al. [32] on type III DES came to the same conclusion. In an experiment study by Gabriele et al. [33], FTIR and NMR characterization showed that ChCl-glycol DES structure remained intact with the presence of water up to 50 %w (around 80 %v). Such indication could be ground for the use of aqueous DES solution (DES mixed with water) to address the high viscosity problem.

Moreover, the study regarding the use of ChCl-MEA DES has only been limited to the measurement of its CO_2 absorption capacity in singular conditions [17,34,35]. There is lack of study on the effect of operating parameters such as temperature and pressure on ChCl-MEA DES absorption performance. Likewise, while the mixing of water into DES has been proposed by other studies, the behavior of aqueous DES solution with various water contents has not been studied under different operating parameters.

With the potential for a more efficient CO_2 absorption in mind, it becomes important to study the characteristics and behavior of CO_2 absorption by ChCl-MEA DES in moderate operating conditions that could be achieved without the high consumption of energy. Therefore, the aim of this study is to evaluate the CO_2 absorption capacity and kinetic of ChCl-MEA DES in various operating pressure and temperatures, as well as the effect of water mixing that was expected to lower absorbent viscosity and aid in mass transfer. These objectives shall be obtained through physical experiments, model fitting, and material behavior prediction based on the developed model. Response surface methodology is chosen due to its ability to analyze the effect of individual factors, the effect of interaction between factors towards a chosen response, and system optimization [36–39]. Analysis of the gas after absorption equilibrium would also be conducted to complete and verify the absorbents' selectivity.

2. Material and method

2.1. Materials

The chemicals used in this experiment consist of 99.5 % purity monoethanolamine (MEA) purchased from Chinese chemical vendor Aladdin-e. This material is used without further purification. The 99 % purity choline chloride (ChCl) purchased from Aladdin-e was also utilized. It was dried in an oven for 24 h at 105 °C to remove any water content before using.

The gas used is model syngas with the composition being: CO_2 (40 % v), H_2 (30 %v), CH_4 (5 %v), CO (5 %v), and N_2 (20 %v). This composition is chosen as an approximation of the outlet gas of air gasification after going through water-gas shift reactor [40], as well as resembling syngas from biomass supercritical water gasification (SCWG) [41]. The model syngas was purchased through a commercial gas vendor in China and used without further purification.

2.2. DES preparation

The DES composition used in this experiment was 1:5 mol ratio ChCl to MEA. The mole ratio 1:5 was chosen since it is one of the successfully prepared DES with most balanced ratios between ChCl and MEA, as reported in a study by Mjalli et al. [26]. Li et al. also found that 1:5 is the optimum mole ratio when considering ChCl to MEA mole ratios between 1:2 to 1:6 [42]. It was prepared by first weighing each material and then mixing the appropriate amount of ChCl and MEA to obtain 1:5 mol ratio. This mixture was then placed into a beaker, sealed with parafilm, and placed on a magnetic hot plate with stirrer. The mix was heated at 60 °C and stirred at 300 rpm for 3 h. Afterwards, the resulting clear white homogenous liquid is left to rest for 48 h in a sealed container. If phase stability was obtained, the DES was used for the experiments. Water content measurement using Karl Fischer titration determined that the prepared neat DES has an initial water content of around 3.72 %v.

Neat DES (0 %v water addition) would be used without any further modifications, while the aqueous DES were prepared by adding the appropriate amount of water into neat DES. This was done by mixing certain volumes of neat DES and deionized water to create aqueous DES mixtures containing 25 %v and 50 %v water. The liquids were measured using micropipette and mixed in a beaker. The mixed liquid was then heated at 60 °C and stirred at 300 rpm for 3 h to ensure throughout mixing. The resulting aqueous DES was stored in a sealed container prior to being used in the experiments.

2.3. Experiment setup

The absorption experiment was conducted using a 100 mL stainless steel tubular batch reactor with furnace and magnetic stirrer. The inlet valve to the reactor was connected to a model syngas tank and the outlet valve lead to a needle valve for gas sampling into gas bags. The complete experiment setting is displayed in Fig. 1.

During experiment run, the reactor was first filled with 4.5 mL of selected absorbent. Then the reactor was sealed and vacuum pumped to remove excess air. The sealed reactor was then heated to the desired temperature and model syngas was injected into the reactor until the target initial pressure of either 5.0, 7.5, or 10.0 bar was reached. Immediately after model gas injection, the stirrer was turned on at 300 rpm. The initial reactor pressure and reactor pressure were logged at intervals of every 1 min for the first 10 min, and every 5 min until no pressure change was detected within 30 min of observation, up to the accuracy of 0.01 bar. At the end of each experiment run, gas sample was collected from an outlet valve and analyzed for composition using GC-9790 gas chromatography from Zhejiang Fuli Analytical Instrument Co. Ltd. It is equipped with a thermal conductivity detector (TCD) packed column and run with helium as carrier gas at 30 mL/min flow.
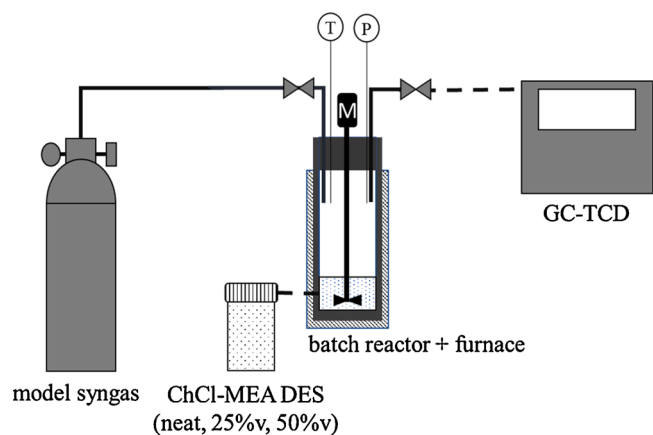
Fig. 1. Batch absorption experiment setting.

2.4. Experiment design and data analysis

The experiment runs and subsequent data analysis were designed according to the Response Surface Method (RSM) using Box-Behnken design of experiment. The Box-Behnken design of experiment is chosen, as opposed to the central composite design of experiment, due to its relative simplicity and efficiency [43]. Box-Behnken design of experiment aims to predict the value of a response using the least amount of experiment. Response value for the data point in the condition in which no experiment was conducted could be obtained using statistical analysis by extrapolation from 2 adjacent data points which would always be present as part of the experiment design [43]. The range of the studied factors is listed in Table 1 below.

The temperature range was capped at 80 °C to minimize water evaporation. While water content was capped at 50 %v to ensure DES structure remained intact, as suggested by previous studies [30,32,33]. Each experiment run listed in Table 1 was duplicated at least twice. The central data point (60 °C, 7.5 bar, 25 % water content) was repeated 3 times according to the Box-Behnken design requirement used. The experiment output was pressure decrease due to CO_2 absorption by the DES. It was converted to three types of responses: CO_2 absorption capacity, which is expressed as mol CO_2 absorbed per mol of DES in the solvent; CO_2 absorption rate, which is obtained from CO_2 absorption capacity divided by time to reach equilibrium; and gas concentration from GC-TCD results. It is worth noting that the mol amount of DES present in each experiment run might be different depending on amount of water mixed with DES (0, 25, and 50 %v). The values of total CO_2 absorbed were then normalized per mol of DES in the respective absorbents. CO_2 solubility in water was not considered since its values within the studied factor range were negligible compared to the values of CO_2 absorption capacity by DES and its aqueous solutions [44].

For analysis of CO_2 absorption capacity and rate, the data obtained from the experiment and calculations were first subjected to ANOVA (analysis of variance) to gauge its f-value and p-value. Should the data be proven to be statistically meaningful, the significant variables are analyzed using response surface methodology. These results could be displayed in the form of an equation and pareto chart of standardized effect that measures the extent of effect of each factor towards the behavior of the response. The Pareto chart would determine which factors or interaction between factors are statistically significant and

should be studied further.

The equation would be used to generate surface plots which displays the interaction between all three factors and their effect towards the response. This chart is useful to evaluate the overall behavior of the system as well as finding the value of factors that corresponds with an optimum value of response within the studied range.

Gas analysis is done by measuring the effect of changes in operating conditions towards the amount of each gas species in model syngas absorbed by the absorbent. This is done using the calculation for main effect of operating pressure and temperature against the amount of each gas species absorbed in every mol of absorbent.

3. Result and discussion

3.1. Experiment results

Batch experiment utilizing the setup explained in Section 2.3 were conducted with runs designed using Box-Behnken DOE as explained in Section 2.4. The summary of the results from the physical experiment is listed in Table 2. CO_2 absorption capacity is measured in mols of CO_2 absorbed in every mol of DES in the absorbent (mol-CO_2/mol-DES), while CO_2 absorption rate is stated in mol of CO_2 absorbed per 1000 mol of DES in absorbent every second (mol-CO_2/kmol-DES•s). Each response value is an average of 2 experiment runs.

Data from Table 2 was then plotted to a bar graph as seen in Fig. 2. This step is done to qualitatively gauge the tendency of the data. Table 2 also shows that the maximum pressure decreases observed in all runs was around 37 %, below the theoretical 40 % pressure decrease if all of the CO_2 in the model syngas was absorbed. This indicates that the absorption process has stopped due to the system reaching equilibrium, as opposed to the depletion of CO_2 in the gas phase.

From Fig. 2, a few tendencies appeared to be observable. The first is the positive effect of water content towards the CO_2 absorption capacity, which is measured in mol CO_2 per mol of DES present in the absorbent. Temperature appeared to have negative effect on CO_2 absorption capacity. Lastly, pressure appeared to have a positive effect on CO_2 absorption capacity. These observations seemed to be consistent for all data points in the studied range.

To further analyze the data for effect quantification and interaction between the factors, the data is evaluated by statistical means to check for its reliability before being analyzed using response surface method. The details of these steps are explained in the next parts. The analysis is divided into analysis of CO_2 absorption capacity and CO_2 absorption rate of ChCl-MEA DES.

Table 1
Range of studied factors.

No.	Factors	Low Value	Middle Value	High Value
1	Temperature (°C)	40	60.0	80
2	Initial Pressure (bar)	5	7.5	10
3	Water Content (%v)	0	25.0	50

Table 2
Experiment design based on Box-Behnken DoE and the responses.

Factor 1	Factor 2	Factor 3	Responses	
Water Content (%v)	Temperature (°C)	Initial Pressure (bar)	CO_2 Absorption Capacity (mol-CO_2/mol-DES)	CO_2 Absorption Rate (mol-CO_2/kmol-DES•s)
0	40	7.5	0.159	0.776
0	60	5.0	0.091	0.447
0	60	10.0	0.198	1.098
0	80	7.5	0.132	0.654
25	40	5.0	0.140	0.585
25	40	10.0	0.284	1.577
25	60	7.5	0.188	0.782
25	60	7.5	0.186	0.751
25	60	7.5	0.188	0.782
25	80	5.0	0.120	0.667
25	80	10.0	0.224	1.247
50	40	7.5	0.315	1.312
50	60	5.0	0.189	0.917
50	60	10.0	0.372	2.071
50	80	7.5	0.255	1.235

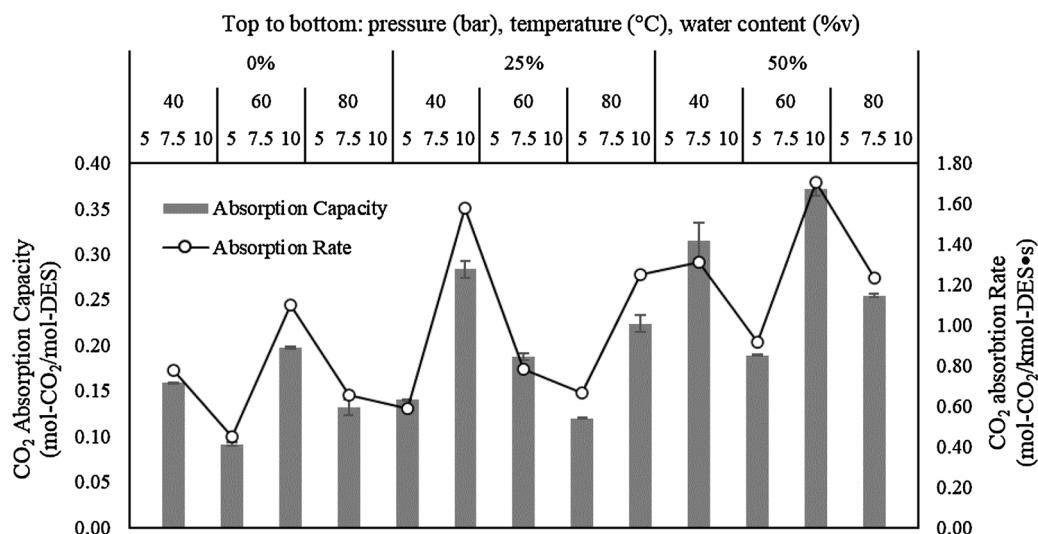Top to bottom: pressure (bar), temperature (°C), water content (%v)

Fig. 2. Graphical representation of physical experiment data results.

3.2. CO_2 absorption capacity

The experiment data for CO_2 absorption capacity was first analyzed for their reliability using Analysis of Variance (ANOVA). The result of the ANOVA is presented in the pareto chart of standardized effect as seen in Fig. 3 below.

The pareto chart in Fig. 3 was created with the data analyzed in the previous section. The confidence level is 95 % ($\alpha = 0.05$) and is shown as the cutoff line at the standardized effect value of 2.31. From Fig. 3, it could be noticed that effect of water content and initial operating pressure are very significant to the CO_2 absorption capacity by DES. Operating temperature is also statistically significant, even though its effect was predicted to be not as pronounced as water content and initial operating pressure. The significance of each factor would be discussed further in the next section. Fig. 3 also shows the previously discussed factor interactions of pressure*water-content (P*W), which fell just below the cutoff line but shall be included in subsequent discussions as it might become significant with further reduction of the model.

After excluding non-significant terms P*T and T*W, the model reached adjusted R-squared value of 94.82 % and R-squared predicted value of 90.99 %. When compared to R-squared value of 96.30 %, the data with reduced terms is considered to provide sufficient fit to the model. The adjusted model is then expressed into an equation as seen in Eq. 1 below.
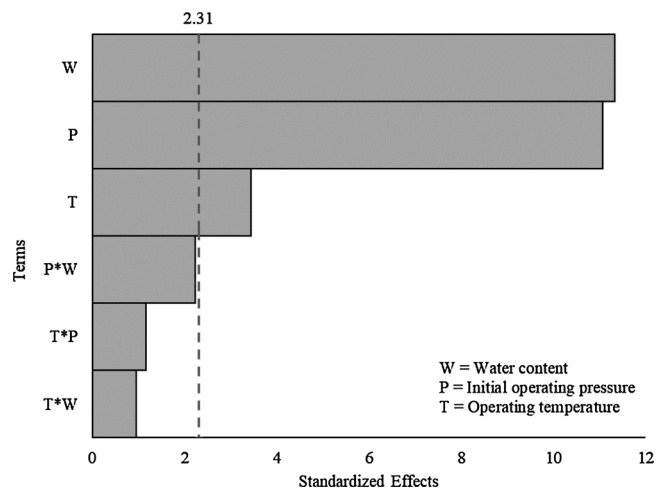
$$CO_2 \text{ Capacity} = 0.0525 - 0.001043\ T + 0.01920\ P + 0.00046\ W + 0.000306\ P*W \quad (1)$$

The symbols in Eq. 1 are the same as those used in Fig.3, where T = operating temperature, P = initial operating pressure, and P*W = interaction between initial operating pressure and water content. Using Eq. 1, surface plots were then generated for every temperature investigated in this study. They are displayed in Fig. 4(a), (b), and (c).

The effect of temperature towards CO_2 absorption capacity within the studied range could be evaluated by comparing Fig. 4(a), (b), and (c). It could be seen that CO_2 absorption capacity decreased with temperature. While an increase in initial operating pressure produced an increase in CO_2 absorption capacity. These results suggested that the behavior of CO_2 absorption by ChCl-MEA DES is consistent with the behavior of physical absorbents. It is massively influenced by pressure in a positive way, while negatively influenced by pressure. This is in accordance with Henry's Law that states that the absorption capacity is for physical absorbent is proportional to the partial pressure of the absorbate gas [45]. For comparison, chemical absorption such as the mechanism taking place with amine solution occurs through chemical reaction [46]. As such, absorption performance would increase with temperature [47], while pressure would have little effect on the absorption capacity.

This could bring potential benefits such as the ability to utilize processes with high syngas outlet pressure, such as from SGWG or pre-combustion syngas from IGCC power plants [48]. Desorption and regeneration of physical solvent is done by flashing (dropping the pressure to release absorbed gases). Compared to chemical solvents such as the amine, it provides benefits such as energy efficiency due to the absence of heating needed. This could also lead to increased cost effectiveness from the minimalization of solvent loss or degradation due to heating, which is the main problem with amine processes at the moment [49].

The effect of water content on CO_2 absorption by ChCl-MEA DES could also be studied from Fig. 4. It appears that the CO_2 absorption capacity per mol of DES increased with higher water content in DES. In Fig. 4a, DES with 50 %v water had between 0.206 – 0.379 mol-CO_2/mol-DES capacity, on average around 1.5 times that of DES with 25 %v water mixed and nearly twice that of neat DES (0 %v of water) for absorption process at the same initial pressure. The same trend could also be observed in Fig. 4(b) and (c), indicating that this effect applies all across the studied temperature range.
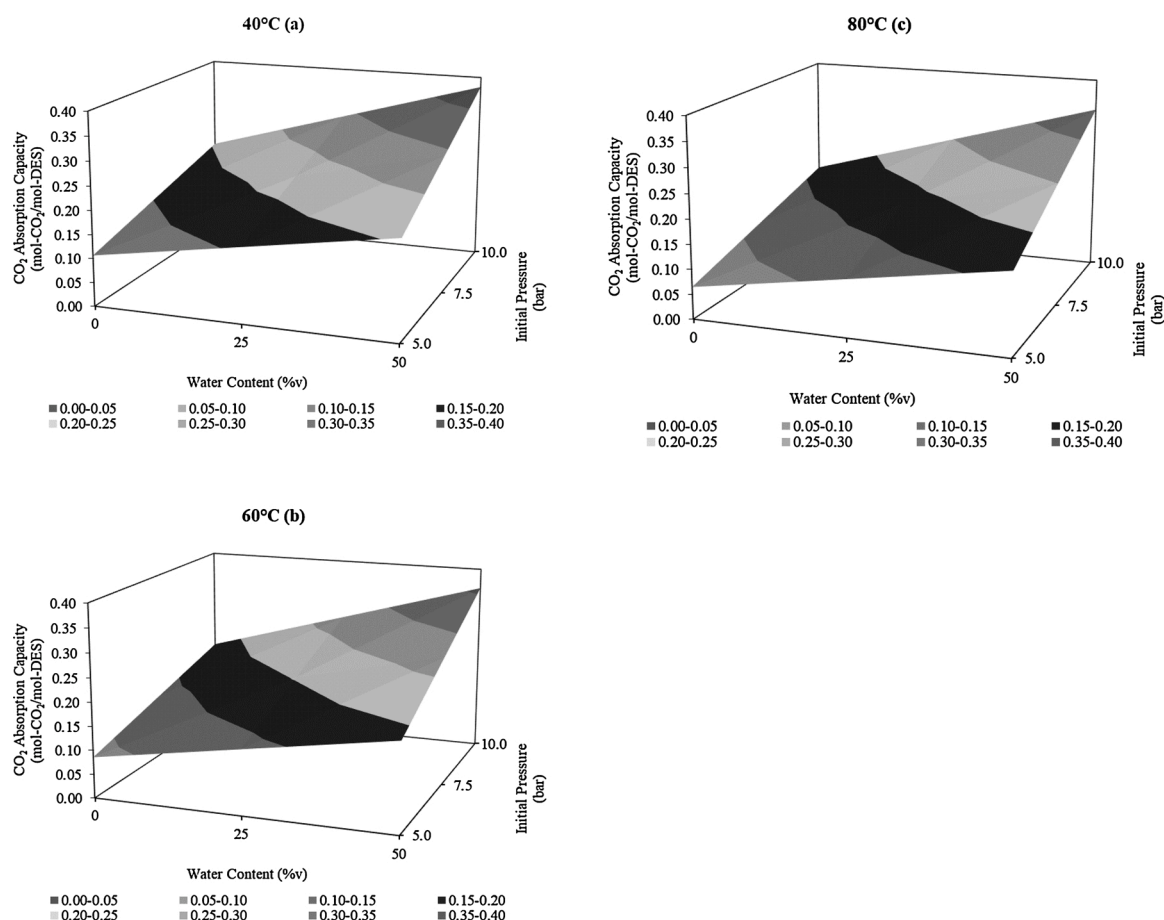

Fig. 3. Pareto chart of standardized effect for CO_2 absorption capacity.

40°C (a)

80°C (c)

60°C (b)

Fig. 4. Surface plot of CO_2 absorption capacity vs water content, initial pressure at 40 °C (a), 60 °C (b), and 80 °C (c).

It must be noticed that this does not mean that the same volume of solvent with more water in it would dissolve more CO_2. Instead it indicates that every mol of DES, when placed in a solution with more water in it, was able to dissolve more CO_2 compared to when placed in neat DES with no water content. When comparing the total amount of CO_2 dissolved by equal volume of solvents, neat DES still dissolves more CO_2 compared to DES with high water content in it.

This phenomenon might be explained by the presences of water having a beneficial effect in terms of mass transfer and spreading of DES, making it easier for DES molecules in aqueous solution to come in contact with CO_2 and for dissolution to happen. This in turn allows more DES molecules in aqueous solution to take part in CO_2 absorption compared to molecules in neat DES.

Fig. 3 suggested that the interaction between initial pressure and water content (P*W) might have a slightly noticeable effect. This is shown in the different slope along the line of pressure between absorption with neat DES and DES with 50 %v water content. For absorption with neat DES, the increase of initial pressure from 5 bar to 10 bar resulted in a 0.096 mol-CO_2/mol-DES capacity increase. While for absorption with DES with 50 %v water content, the same range of pressure increase resulted in 0.172 mol-CO_2/mol-DES capacity increase.

It seems that at higher pressure, increasing initial operating pressure result in higher upsurge of CO_2 absorption capacity. This phenomenon could be due to the lower viscosity of water compared to ChCl-MEA DES at a given temperature. Hence, the presence of high amount of water would allow pressure to more easily drive contact between CO_2 and DES, resulting in higher CO_2 absorption capacity.

This might lead to the potential for process flexibility where absorption efficiency could be increased by simply mixing water into the DES without changing the system pressure. However, it must also be

considered that mixing more water into the DES would also cause an increase in the volume of absorbent needed. This would mean that in an industrial setting, more absorbent liquid needs to be pumped through the system, possibly increase the pumping duty required. Considering that pump duty is usually small compared to other utilities in the system, this approach is still worth investigating further.

It should also be noted that the absence of a global optimum point in Fig. 4(a), (b), and (c) suggested that the study range could be expanded, with experiments at higher initial pressure seemingly being the most potential method to provide higher CO_2 absorption capacity.

3.3. Result comparison with other studies

The equation generated using statistical analyses allows for prediction of CO_2 absorption capacity on operating conditions and water content that were not conducted in this study. For example, a prediction for CO_2 absorption capacity of neat ChCl-MEA 1:5 DES at (30 °C, 1 bar) yielded a value of 0.044 mol-CO_2/mol-DES, which is in a good agreement with the result reported by Li et al. at 0.043 mol-CO_2/mol-DES [42].

A recent study by Sarmad, et al. [50] investigated CO_2 absorption capacity of ChCl-MEA 1:7 DES at absorption pressures from 10 bar to 20 bar. The obtained value for ChCl-MEA 1:7 DES CO_2 absorption capacity value at (25 °C, 10 bar) was 0.210 mol-CO_2/mol-DES. It is similar to the value obtained in this study at 0.203 mol-CO_2/mol-DES. The difference might be caused by the difference in operating temperature, 40 °C in this study and 25 °C in the study by Sarmad et al. The difference in mol ratio between 1:5 in this study and 1:7 in the study by Sarmad et al. is not expected to produce significant difference in CO_2 absorption capacity, as found by Li et al. [42]. Experiment data by Sarmad et al [50]

at (25 °C, 20 bar) produced a CO_2 absorption capacity value of 0.290 mol-CO_2/mol-DES, which is similar to the 0.301 mol-CO_2/mol-DES calculated with the equation generated in this study.

The maximum CO_2 absorption capacity obtained in this study range, 0.379 mol-CO_2/mol-absorbent (DES), is lower than the maximum 0.5 mol-CO_2/mol-absorbent (amine) from a previous study using conventional MEA solution [7]. In the case of DES however, this CO_2 absorption capacity value could potentially be increased further by raising the operating pressure as suggested by Fig. 4. This characteristic could be suitable for utilization with thermochemical processes that produced syngas at high pressure, such as supercritical water gasification that operates at around 230 – 350 bar [51].

3.4. CO_2 absorption kinetics

The analysis for CO_2 absorption rate of ChCl-MEA DES follows the same steps as CO_2 absorption capacity discussed in Section 3.2. ANOVA results for the CO_2 absorption rate response is presented in the Pareto Chart of Standardized Effect in figure below

Fig. 5. Pareto chart of standardized effect for CO_2 absorption rate

Based on the information from Fig. 10, the individual factors that have significant effect towards CO_2 absorption rate are initial pressure and water content. No interaction between factors caused significant effect to the response, therefore only effect of individual factors is analyzed. The adjusted R-squared value after discarding non-significant factors was 87.09 %, adequately close to the R-squared value of 88.93 %. The relationship between significant factors and response for CO_2 absorption rate could be expressed with Eq. 2 listed below. The symbols used in Eq. 2 are in accordance with those used in Fig. 5, with P = initial operating pressure and W = water content.

$$CO_2 \text{ Absorption Rate} = -0.434 + 0.1507 \, P + 0.01098 \, W \qquad (2)$$

From these analyses, the effect of initial operating pressure and water content towards CO_2 absorption rate by ChCl-MEA DES and its aqueous solutions could be predicted. Using Eq. (2), CO_2 absorption rate surface plots for each studied temperature could be generated. Since Eq. 2 implies that the effect of temperature is insignificant towards CO_2 absorption rate, only one surface plot shall be displayed, and it applies for the entire range of studied temperature.

Fig. 6 shows that initial operating pressure has a positive effect on CO_2 absorption rate by ChCl-MEA DES for all water content. Using the two-film theory, this phenomenon could be explained as higher pressure thinning the film in the boundary layer between gas and liquid phase. This in turn makes for a faster transfer of CO_2 molecules from gas to liquid phase [52].
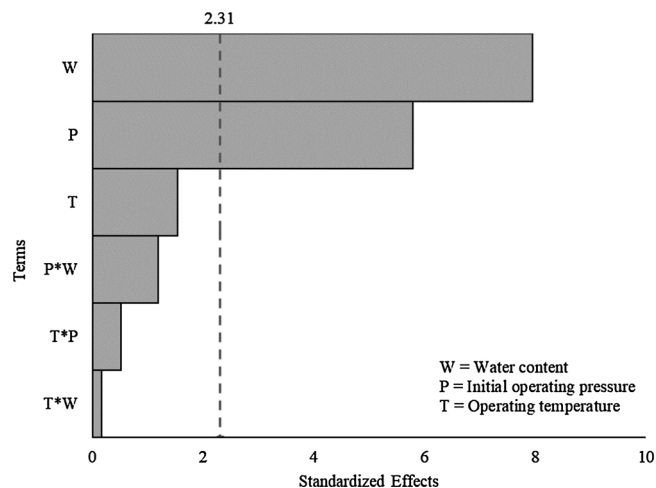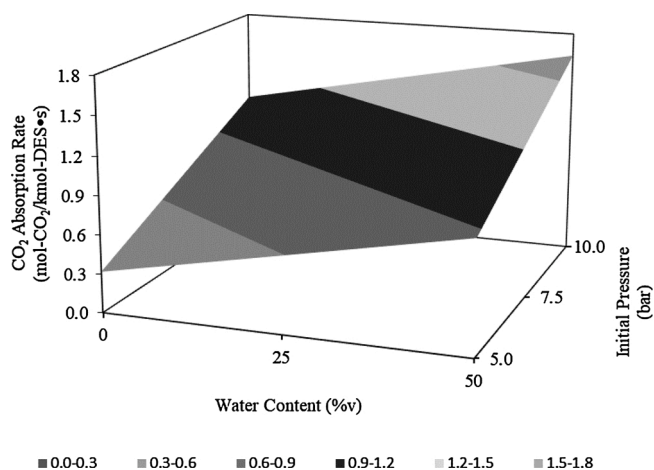

Fig. 6. Surface plot of CO_2 absorption rate vs water content, initial pressure.

water content in ChCl-MEA DES also had a positive effect towards the absorbent's CO_2 absorption rate. With CO_2 absorption rate value at all conditions following the order of DES with 50 %v water > DES with 25 %v water > neat DES. This improvement might come from the presence of water that has lower viscosity compared to ChCl-MEA DES, lowering the overall viscosity of the solution and making it easier for CO_2 to come in contact with ChCl-MEA DES molecules.

However, as suggested by Eq. 2, there is no effect of interaction between pressure and water content. The uniform slope for pressure increases from 5 bar to 10 bar, in which CO_2 absorption rate for DES with 0 %v, 25 %v, and 50 %v water content increase of around 0.753 mol-CO_2/kmol-DES•s, indicate that pressure affects DES the same way regardless of water content. It could mean that while higher water content helps with DES spread and providing more contact between CO_2 and DES, the mechanism of absorption remains the same. This is in good agreement with the find by Hammond et al. that suggested that DES is able to stay stable and intact when mixed with up to 50 %v of water [31].

In Fig. 6, the large slope on the initial pressure side indicates that increasing initial operating pressure of the absorption system would provide better results in increasing CO_2 absorption rate, as opposed to increasing water content. However, increasing system pressure is usually more complex. Therefore, it is worth considering increasing DES water content as an alternative to increasing the absorbent's CO_2 absorption rate. Similar to the contour plot for CO_2 absorption capacity in Fig. 4, the absence of an optimum point in Fig. 6 suggests that an expansion of the study towards higher pressure and water content could be beneficial.

3.5. Gas analysis

Analysis of the output gas was done to determine the which gas species in the model syngas is involved with the absorption process and their response towards changes in the operating conditions, i.e. temperature and pressure. The gas analysis is done using calculations for the main effect of individual factors towards a response. The factors considered are operating temperature and initial operating pressure, while the response is the mol of gas absorbed by 1 mol of DES for every gas species in the model syngas. The analysis was done using DES with 25 %v water content. The results are shown in Figs. 7 and 8 below.

Fig. 7 shows the effect of initial operating temperature towards the amount of absorbed gas for every gas species in the model syngas. A tendency of increased absorption of gases were observed with the increase in initial operating pressure. Pressure increase from 5 bar to 10 bar resulted in the amount of CO_2 absorbed doubling, from 0.14 to 0.28 mol-CO_2/mol-DES. The amount of H_2 absorbed also increased from

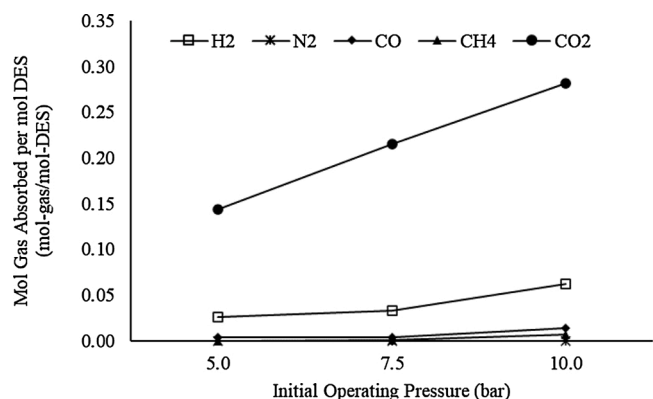**Fig. 5.** Pareto chart of standardized effect for CO_2 absorption rate.

Fig. 7. Main effect of initial operating pressure towards the amount of gas absorbed by 1 mol of DES for every gas species.
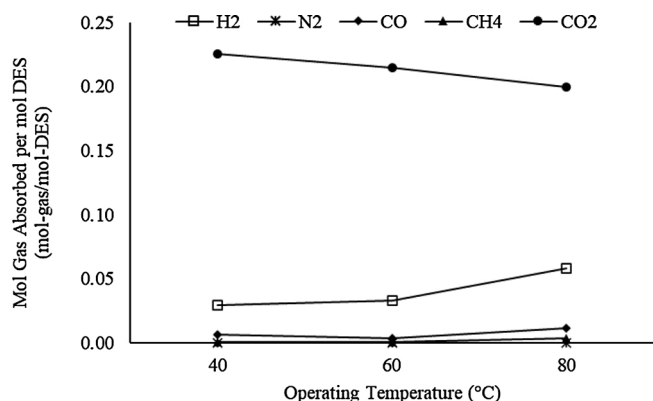

Fig. 8. Main effect of operating temperature towards the amount of gas absorbed by 1 mol of DES for every gas species.

0.02 to 0.06 mol-H_2/mol-DES for the same pressure increase. Absorption of other gas species also saw slight increases, although all of them were below 0.013 mol-gas/mol-DES.

In terms of CO_2 concentration in the outlet gas, absorption process increased from 5.0 to 10.0 bar resulted in the CO_2 molar concentration to dip from 82.79 % to 77.13 %; respectively. This was mostly due to the observed increase in amount of absorbed H_2.

Fig. 8 displays the main effect of operating temperature towards the amount of gas absorbed by DES for every gas species in model syngas. The figure indicates a decrease in absorbent selectivity towards CO_2, marked by a decline in the amount of CO_2 absorbed along with increasing operating temperature. From 40 °C to 80 °C, amount of CO_2 absorbed changed from 0.22 to 0.20 mol-CO_2/mol-DES. Absorption of other gas species also increased somewhat with the increase of temperature. The biggest increase was observed for H_2, with the amount absorbed increasing from 0.03 to 0.06 mol-H_2/mol-DES with operating temperature increase from 40 °C to 80 °C. It appears that increase in temperature enhances the H_2 absorption, even though the exact mechanism needs to be investigated further.

Operating temperature of 40 °C, 60 °C, and 80 °C resulted in CO_2 concentration in outlet gas of 86.19 %, 85.14 %, and 73.09 %; respectively. This result combined with Fig. 4 suggest that lower temperature result in better CO_2 absorption by ChCl-MEA DES as it produces higher CO_2 absorption capacity as well as higher CO_2 concentration in the outlet gas.

4. Conclusion and suggestion

Results of this study found that CO_2 absorption by ChCl-MEA DES

and its aqueous solutions was positively affected by initial operating pressure and negatively affected by temperature. These results are consistent with the prediction that the dominant mode of CO_2 absorption by ChCl-MEA DES is by physical absorption.

High water content, low temperature, and high pressure were found to increase ChCl-MEA DES CO_2 absorption capacity per-mol of DES. This phenomenon might be explained by the presence of water easing mass transfer of CO_2 into the DES. The highest CO_2 absorption capacity obtained in this study was 0.379 mol-CO_2/mol-DES from absorption using DES with 50 %v water at 40 °C, 10 bar.

Study into CO_2 absorption rate of ChCl-MEA DES found that it is positively influenced by pressure and water content. However, these two factors did not interact to create a synergic effect, as water content up to 50 %v seems to assist with absorbent spreading but did not change the absorption mechanism.

Gas analysis suggests that higher amount of CO_2 was absorbed at higher absorption pressure. However, the CO_2 concentration decreased from 85.14 % to 77.13 % with pressure increase from 5 bar to 10 bar, mainly due to increased amount H_2 absorbed. While absorption temperature seems to negatively affect the amount of CO_2 absorbed. This result means that CO_2 absorption by ChCl-MEA DES works better at lower temperature, as it produces both higher CO_2 absorption capacity as well as CO_2 concentration in outlet gas.

CRediT authorship contribution statement

Haryo Wibowo: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft. **Wenjuan Liao:** Conceptualization, Resources, Validation. **Xuanyou Zhou:** Formal analysis, Resources, Data curation. **Caimeng Yu:** Validation, Resources, Investigation. **Dicka Ar Rahim:** Conceptualization, Methodology, Investigation. **Dwi Hantoko:** Methodology, Visualization, Writing - review & editing. **Huan Qun:** Resources, Investigation, Writing - review & editing. **Mi Yan:** Visualization, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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