



## Research article

 $H_2S$ – $CO_2$  gas separation with ionic liquids on low ratio of  $H_2S/CO_2$ Tri Partono Adhi<sup>a</sup>, Yohanes Andre Situmorang<sup>b</sup>, Haryo Pandu Winoto<sup>a</sup>, Danu Ariono<sup>a</sup>, Diannisa Septiana<sup>a</sup>, Patricia Imanuela<sup>a</sup>, Antonius Indarto<sup>a,b,\*</sup><sup>a</sup> Department of Chemical Engineering, Institut Teknologi Bandung, Labtek X, Kampus ITB, Jalan Ganesha 10, Bandung, 40132, Indonesia<sup>b</sup> Department of Bioenergy Engineering and Chemurgy, Institut Teknologi Bandung, Jalan Let. Jen. Purn. Dr. (HC), Mashudi No. 1, Sumedang, Indonesia

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## ABSTRACT

Acid gas removal, especially  $H_2S$  and  $CO_2$ , is an essential process in natural gas processing. In this research, 1-butyl-3-methylimidazolium bromide [bmim][Br] ionic liquid was analyzed as a hydrophobic solvent with high selectivity to  $H_2S$  as an environmentally friendly solvent to absorb acid gas from natural gas with low  $H_2S/CO_2$  concentration in ambient temperature and pressure. The absorption performance of pure [bmim][Br] ionic liquid was compared with various amine solutions, such as monoethanolamine (MEA), triethanolamine (TEA), and methyldiethanolamine (MDEA), as well as the mixture of [bmim][Br]-MDEA with various concentration. As a result, pure [bmim][Br] ionic liquid had high selectivity to  $H_2S$  compared with conventional amine solutions. In addition, the mixture of [bmim][Br]-MDEA with the mass ratio of 1:3 provided the highest  $H_2S/CO_2$  selectivity of 6.2 in certain absorption conditions due to free tertiary amine attached in the cations of ionic liquids that can attract more  $H_2S$  to its functional site.

## 1. Introduction

Even though fossil fuels have been predicted to decline, they have remained the primary energy source for years. Natural gas is ranked the third most consumed fossil fuel after oil and coal, with 24% of world consumption in 2015. Its production is moderately projected to peak at 140–217 EJ/y between 2025 and 2066 [1]. Based on current production and consumption trends, the energy consumption share from natural gas is predicted to increase to 25% of global fossil fuels consumption in 2035 compared with the share of 22% in 2015, making natural gas a substantial energy source [2].

Generally, in natural gas processing, hydrogen sulfide ( $H_2S$ ) and carbon dioxide ( $CO_2$ ) are produced during operation in different concentrations based on location and underground soil characterization of the natural gas sources.  $CO_2$  is a significant greenhouse gas (GHG) that has the most considerable involvement in climate change, and it is typically released from hydrocarbon combustion. In processed streams,  $CO_2$  is categorized as acid gas that can form acids that corrode pipelines, reactors, and other equipment in the presence of water. Furthermore,  $CO_2$  provides no heating value, so it must be removed to meet gas quality specifications. The level of  $CO_2$  in commercial natural gas is typically limited to be less than 3% [3].

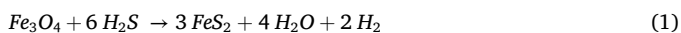
Meanwhile,  $H_2S$  is a toxic, colorless, highly flammable gas and has an odor that is described similarly as a rotten egg. The acid property of this gas also makes it corrosive to the pipeline and could potentially poison the catalyst. From an environmental standpoint, the combustion of fuels containing  $H_2S$  will cause the release of toxic sulfur oxides to the atmosphere, causing acid rain which has adverse impacts on human health [4]. Therefore, removing unacceptable amounts of  $H_2S$  and  $CO_2$  from fossil fuel streams early before their further treatment is essential.

Conventional natural gas processing requires  $H_2S$  and  $CO_2$  to be removed in an acid gas removal unit (AGRU) using aqueous amine absorption processes. In the operations with steam reformer units such as in ammonia production and methanol synthesis processes,  $H_2S$  has to be separated early before the reformer because it will harm the reforming catalyst. Meanwhile,  $CO_2$  that will be more produced by water gas shift reaction in the reformer is separated before ammonia production since high purity of hydrogen is required [5]. Several groups of alkanolamines include monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), and methyldiethanolamine (MDEA) are commonly used for the natural gas sweetening process. However, the amine process application has some disadvantages, especially the loss of amine solution during regeneration, the degradation of amine to form corrosive byproduct, the high pressure for absorption, and the high temperature for desorption lead to expensive process [6].

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For H<sub>2</sub>S removal, other processes can be applied, such as physical adsorption, chemical process, biological method, and electrochemical. Physical adsorption is appropriate to remove H<sub>2</sub>S even at low concentrations using common adsorbents, such as activated carbon, alumina, silica, zeolites, and metal oxides (Zn, Cu, Fe, etc.). The chemical process like the Fe<sub>3</sub>O<sub>4</sub> involving reaction can be applied for H<sub>2</sub>S removal at high temperature and high concentration of H<sub>2</sub>S with the reaction occurs as follow:



The biological method was used to convert dissolved H<sub>2</sub>S to elemental sulfur using sulfur-oxidizing bacteria such as Thiobacillus. A similar concept was applied in liquid redox system that applying chemicals instead of microorganism [7,8]. In comparison, the indirect electrolysis method can be a very promising method that converts H<sub>2</sub>S in gas streams to produce both sulfur and hydrogen simultaneously using vanadium dioxide in acidic aqueous media [9].

For CO<sub>2</sub> removal, there are two most favorable routes, i.e., chemical and physical absorption. The most popular one is chemical absorption using amine solutions with high operating costs. While physical absorption, that uses a solvent such as methanol (Rectisol), polyethylene glycol-dimethyl ether/PEG-DME (Selexol), n-methyl-2-pyrrolidone/NMP (Purisol), and propylene carbonate/PC (Fluor) are available at low capital and operating cost. This method applies the solubility of CO<sub>2</sub> in the solvent as the driving force. Generally, the solubility increases with the increase of pressure and the decrease of temperature of the absorption process. Thus, the optimum condition for the CO<sub>2</sub> absorption process occurs at high pressure and low temperature [10,11].

In addition, polymeric membranes and pressure swing adsorption (PSA) have also been proven as suitable methods for CO<sub>2</sub> removal. Moreover, solid adsorbent like calcium is being investigated for the CO<sub>2</sub> removal method. However, high-temperature operations for adsorption (600–800 °C) and desorption (over 900 °C) make this method hardly applied as a CO<sub>2</sub> removal method. Moreover, the primary challenge of this method is the deactivation of CaO after the regeneration process due to the increased thickness of CaCO<sub>3</sub> on CaO leads to the decrease of available surface area for carbonation [12,13].

Recently, room temperature ionic liquids (RTILs) have been introduced as attractive materials for CO<sub>2</sub> and H<sub>2</sub>S removal due to their unique properties such as good thermal stability, high polarity, and considerably low vapor pressure. In the natural gas case, the separation of low concentration ratio of H<sub>2</sub>S/CO<sub>2</sub> requires ionic solvents such as RTILs with high selectivity to H<sub>2</sub>S. Ionic liquids have a melting point below 100 °C, so it has a high potential to be used as a solvent for the gas separation process and sulfur recovery due to their unique physico-chemistry properties produced by cation and anion modification [14]. Ionic liquids are proposed as a strong solution to absorb H<sub>2</sub>S regarding CO<sub>2</sub> presence due to the strong bond between H<sub>2</sub>S and RTILs. This specific bond increases gas solubility that promotes H<sub>2</sub>S separation from low soluble molecules such as hydrocarbons and CO<sub>2</sub>. It also encourages H<sub>2</sub>S gas to be released during the regeneration phase to achieve lower energy consumption [15].

Previously, Jalili et al. [16] investigated the comparison of H<sub>2</sub>S and CO<sub>2</sub> solubility in three different 1-butyl-3-methylimidazolium [bmim] ionic liquids, including [bmim][PF<sub>6</sub>], [bmim][BF<sub>4</sub>], and [bmim][Tf<sub>2</sub>N], at temperatures ranging from 30 °C to 70 °C and pressures up to 10 bar. It was found that H<sub>2</sub>S solubility was always higher than CO<sub>2</sub> solubility in those three ionic liquids. Zhang et al. [17] measured the selective separation of H<sub>2</sub>S and CH<sub>4</sub> or H<sub>2</sub>S and CO<sub>2</sub> in neutral and basic ionic liquids. It was found that neutral ionic liquids such as [bmim][TfO] and [bmim][CF<sub>3</sub>SO<sub>3</sub>] can remove H<sub>2</sub>S and CO<sub>2</sub> from natural gas simultaneously. In contrast, basic ionic liquid such as [bmim][Ac] can be potentially used for selective removal of H<sub>2</sub>S from natural gas. Akhmetshina et al. synthesized [bmim][doc] ionic liquid that has H<sub>2</sub>S solubility about 4–5 times higher than conventional ionic liquids [18]. Recently, Zhang et al. [19] developed novel azole-based protic ionic liquids (PILs) 1,5-diazabicyclo [4,3,0] non-5-ene 1,2,4-1H-imidazolide [DBNH][1,-2,4-triaz] that has H<sub>2</sub>S

solubility 20–30 times higher those in conventional ILs. Our previous work [15] proved that [bmim][Br] ionic liquid could selectively separate H<sub>2</sub>S from CO<sub>2</sub> from H<sub>2</sub>S/CO<sub>2</sub> mixture compared with n-methyldiethanolamine (MDEA-1) and the commercial mixture of MDEA and activator (MDEA-2) at ambient temperature and pressure. Table 1 shows H<sub>2</sub>S selectivity of [bmim][Br] ionic liquid compared with MDEA-1 and MDEA-2.

The imidazole-halide based ionic liquids are a complex structure carrying several sites that can specifically respond and interact with a guest molecule. As such, the [bmim][Br] ionic liquid is selected in this study because it is easy to prepare, stable, and has a basic anion [15]. In this research, the selectivity of H<sub>2</sub>S to CO<sub>2</sub> absorption performance using [bmim][Br] ionic liquid was analyzed, especially for natural gas with a low concentration of H<sub>2</sub>S/CO<sub>2</sub>. The amine solutions, such as MEA, TEA, and MDEA, as well as water and the mixture of [bmim][Br]-MDEA solution with the mass ratio of 1:1, 1:3, and 3:1, were also used to compare the absorption performance of [bmim][Br] ionic liquid.

## 2. Experimental

### 2.1. Ionic liquids synthesis

The [bmim][Br] ionic liquid is synthesized in two steps processes include preparation and separation. In the preparation step, about 32 mL of 1-bromobutane and 48 mL of toluene are mixed in a dropping funnel. Later, the mixed solution is weighted and cooled for 2 h. Meanwhile, another mixed solution contains about 14 mL the 1-methylimidazole and 21 mL of toluene are prepared in a three-neck flask. The mass of the solution is measured by weighing the three-neck flask before and after mixing. After the dropping funnel has cooled down, the apparatus is then assembled as visualized in Figure 1.

The mixture of 1-bromobutane and toluene in the dropping funnel is dropped to the three-neck flask while the solution is stirred at 300 rpm for 2.5 h until the dropping funnel is empty. After the mixing process, the three-neck flask is heated to 80 °C while the solution is continued to be stirred at 300 rpm for 12 h. The water bath is filled with ice and oil to keep the temperature stable. The cooling water from the water bath is introduced to the condenser part to condense evaporated liquid. At last, the two-phase solution is formed inside the three-neck-flask containing the ionic liquids at the bottom (yellowish color) and impurities consisting of excess toluene and bromobutane at the top.

In the separation step, a rotary evaporator uses to separate [bmim][Br] ionic liquid from toluene impurities by evaporating the toluene at vacuum pressure so that [bmim][Br] ionic liquid is separated from the two-phase solution. This separation is conducted at 82 °C and 0.27 bar with a mixing speed of 75 rpm. The produced ionic liquid is then characterized by <sup>13</sup>C-NMR and <sup>1</sup>H-NMR.

### 2.2. Gas absorption

In this step, the selectivity and absorption capacity of H<sub>2</sub>S and CO<sub>2</sub> in [bmim][Br] ionic liquid and other solvents are determined. The experiment is done at both ambient temperature and pressure. The feeds are 100%-v of CO<sub>2</sub> gas and 1%-v (CH<sub>4</sub> 99%-v) of H<sub>2</sub>S gas in 10,000 ppm-v. The CO<sub>2</sub> gas absorption is done by introducing 6 mL/min CO<sub>2</sub> gas to a vial that contains 5 mL of absorbent. The excess CO<sub>2</sub> gas is then released into the atmosphere. The same procedure applies to H<sub>2</sub>S gas absorption.

**Table 1.** Solubility and selectivity of H<sub>2</sub>S and CO<sub>2</sub> in ambient temperature and pressure [15].

Solvent	H <sub>2</sub> S (mole/mole)	CO <sub>2</sub> (mole/mole)	Selectivity H <sub>2</sub> S/CO <sub>2</sub>
MDEA-1	0.0183	0.0481	0.38
MDEA-2	0.0206	0.1392	0.15
[bmim][Br]	0.0313	0.0090	3.48

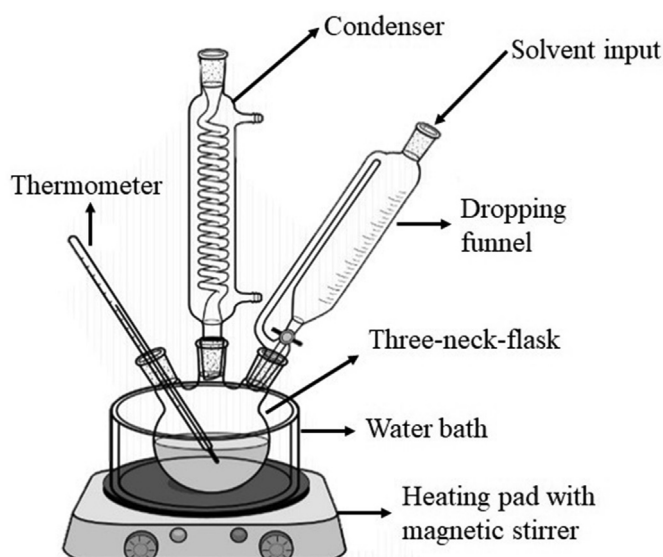


Figure 1. The experimental setup of ionic liquids synthesizing apparatus.

However, after going through the absorbent vial, excess  $H_2S$  gas goes to a vial containing NaOH before being released to the acid chamber. The absorbents used in the gas absorption experiment are (1) pure water, (2) amine solutions, which are MDEA, TEA, and MEA, (3) [bmim][Br] ionic liquid with a range of water content of 0 wt%, 25 wt%, 50 wt%, and 75 wt%, and (4) [bmim][Br]-MDEA mixture with the mass ratio of 1:3, 1:1, and 3:1.

The gravimetry analysis is used to analyze the absorption capacity of  $H_2S$  and  $CO_2$  by weighting solvent mass every 5 min for 60 min for every run. Herein, the solubility of each gas is represented by the total gas mole absorbed every mole solvent and calculated as follows:

$$\frac{\text{Mole of absorbed } i \text{ gas}}{\text{Solvent mole}} = \frac{\text{Solvent mole after absorption} - \text{Solvent mole before absorption}}{\text{Solvent mass}} \times \frac{\text{Mr. gas } i}{\text{Mr. solvent}} \quad (2)$$

where Mr is the molecular weight for each gas and  $i$  represents  $CO_2$  or  $H_2S$ . Meanwhile, the selectivity of  $H_2S/CO_2$  is calculated by dividing  $H_2S$  solubility with  $CO_2$  solubility in the same solvent as follows:

$$\text{Selectivity of } \frac{H_2S}{CO_2} = \frac{\frac{\text{mole of absorbed } H_2S}{\text{Solvent mole}}}{\frac{\text{mole of absorbed } CO_2}{\text{Solvent mole}}} \quad (3)$$

### 3. Results and discussion

#### 3.1. Ionic liquids characterization

##### 3.1.1. $^{13}C$ -NMR analysis

Figure 2 shows the spectrum of  $^{13}C$ -NMR result for [bmim][Br] ionic liquid, which determines how many carbon atoms are present in the molecule. The spectrum shows there were eight carbon atoms in the molecule that were represented by eight peaks. The peaks with carbon chemical shift ( $\delta_C$ ) more than 90 ppm (peak 1–3) represented  $sp^2$  hybridization that illustrates double-bonded carbon. Meanwhile, other peaks with  $\delta_C$  less than 90 ppm (peak 5–9) represented  $sp^3$  hybridization that characterizes single-bonded carbon. The results were matched with the chemical structure of [bmim][Br], which has eight carbon atoms with the exact number of hybridizations as shown by Figure 3. Herein, the structure of [bmim][Br] ionic liquid was illustrated to have three double-bonded carbon atoms ( $sp^2$ ) shown by the bond numbers 2, 3, and 4. In comparison, five single-bonded carbon atoms ( $sp^3$ ) were indicated by the bond numbers 1, 5, 6, 7, and 8. Thus, characterization using  $^{13}C$ -NMR matched the [bmim][Br] structure, and the synthesized product could be confirmed as [bmim][Br] ionic liquid.

##### 3.1.2. $^1H$ -NMR analysis

This characterization was used to determine how many protons (H atoms) and their position inside the molecule. The  $^1H$ -NMR spectrometer could detect the proton chemical shift that represents the spin of the core molecule. The proton chemical shifts were represented by  $\delta_H$  with ppm (part per million) unit. The multiplicity concept ( $n-1$ ) as part of  $^1H$ -NMR characterization could determine how many hydrogen atoms are present in the neighboring cluster.

Figure 4 shows the result of  $^1H$ -NMR characterization on [bmim][Br] ionic liquid. The result shows that the peak number 4 with  $\delta_H$  of 10.1403 ppm was H atom situated at the aromatic cluster and bonded with two N atoms. Meanwhile, the peak number 1 with  $\delta_H$  of 4.0275 ppm was a methyl cluster with a direct bond to an aromatic cluster and the peak number 5 with  $\delta_H$  around 4.2 ppm represented a carbon atom with a bond with the N atom. Moreover, carbon atoms in the structure of ionic liquids were characterized by the peak number 6 with  $\delta_H$  around 1.8

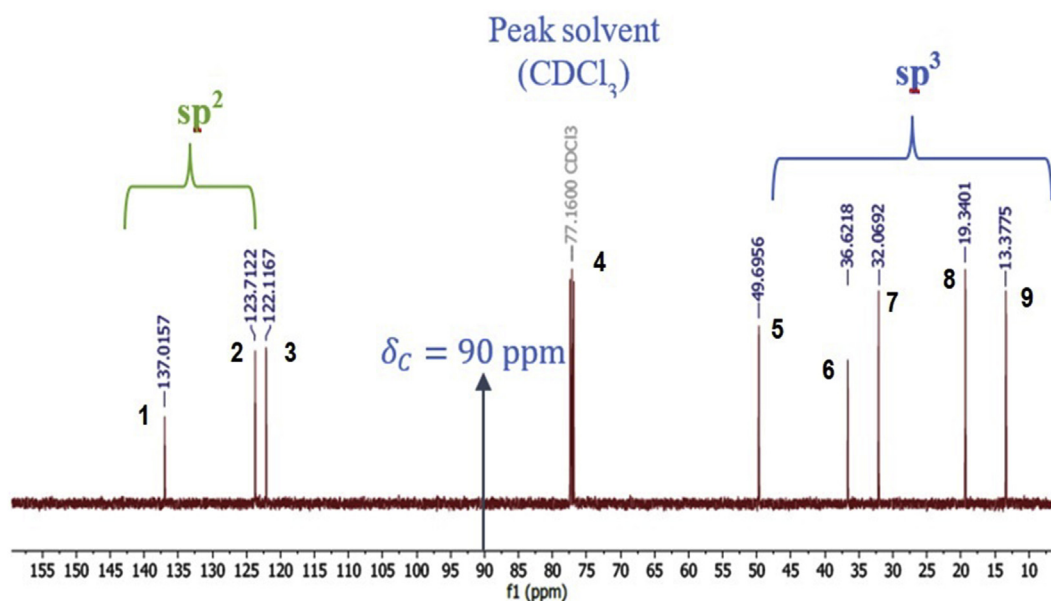


Figure 2.  $^{13}C$ -NMR spectrum result of [bmim][Br] ionic liquid.

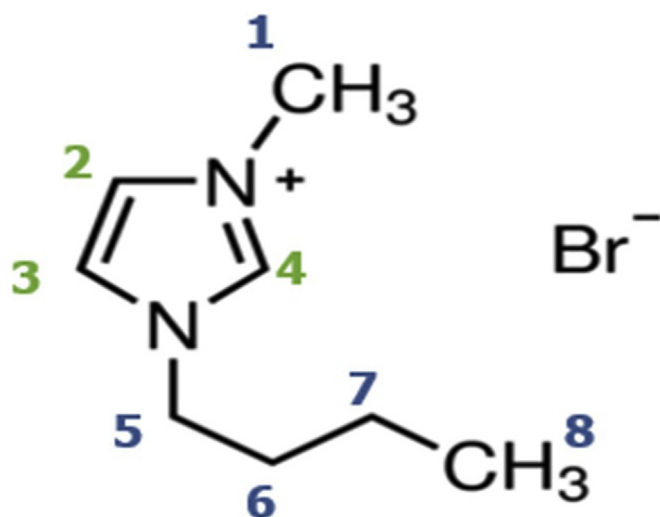


Figure 3. [bmim][Br] chemical structure.

ppm, the peak number 7 with  $\delta_H$  around 1.3 ppm, and the peak number 8 with  $\delta_H$  around 0.8 ppm.

The peak number 4 is situated on the left because the carbon atom is bonded with two nitrogen atoms with high electronegativity. This phenomenon caused a lack of electrons in carbon number 4 and moved further from  $\delta_H = 0$ . Using the multiplicity concept (n-1), the carbon number 8 had three peaks that show two neighboring protons corresponding with H atoms bonded with the carbon number 7. Besides those results, the peak at  $\delta_H = 2.53$  ppm was suspected of belonging to DMSO as impurities. The results of  $^1\text{H-NMR}$  characterization were consistent with [bmim][Br] structure. Thus, it could be concluded that the [bmim][Br] was successfully synthesized with the appropriate form.

### 3.2. Gas absorption in water and amine solution

Figure 5 shows the  $\text{CO}_2$  gas absorption using water and amine solutions that includes pure water/aqua DM, MDEA (7.6 wt%  $\text{H}_2\text{O}$ ), TEA (75.43 wt%  $\text{H}_2\text{O}$ ), and MEA (75.88 wt%  $\text{H}_2\text{O}$ ). The result indicated that all the solutions could absorb  $\text{CO}_2$  gas except pure water in an ambient condition showing the weak bond between  $\text{CO}_2$  and water caused difficulties in absorbing the gas. Specifically,  $\text{CO}_2$  has poor solubility in water at low operating pressure, leading to a high amount of water required to absorb a small amount of  $\text{CO}_2$ . It is well known that the solubility of  $\text{CO}_2$  in water increases by increasing the operating pressure and lowering the operating temperature [20,21].

In comparison, TEA and MEA also have poor  $\text{CO}_2$  absorption performance since they could not react directly with  $\text{CO}_2$ . Their chemical structure forces the  $\text{CO}_2$  to react firstly with water and form carbonic acid before reacting with the alkanolamine group. In contrast, the chemical structure of MDEA enables it to react directly with  $\text{CO}_2$  so it has an exponential absorption profile in absorbing  $\text{CO}_2$  in 60 min compared with other amine solutions. Moreover, the low water content of MDEA did not interfere with the gas absorption significantly [22]. In addition, Kim et al. [23] said that at varied temperatures,  $\text{CO}_2$  mole/MEA mole is much higher than  $\text{CO}_2$  mole/TEA mole, making  $\text{CO}_2$  have a higher solubility in MEA than with TEA.

Meanwhile,  $\text{H}_2\text{S}$  absorption using pure water, MDEA (7.6 wt%  $\text{H}_2\text{O}$ ), TEA (75.43 wt%  $\text{H}_2\text{O}$ ), and MEA (75.88 wt%  $\text{H}_2\text{O}$ ) are shown in Figure 6. It can be seen that  $\text{H}_2\text{S}$  is only absorbed by amine solution because the instant reaction occurs between  $\text{H}_2\text{S}$  and the primary, secondary, and tertiary amine solutions [24]. However, the hydroxyl cluster in amine solutions tends to pull electrons that inhibit nitrogen in the amine cluster from binding with  $\text{H}_2\text{S}$  [25]. As a result, TEA with the highest hydroxyl cluster absorbed the least  $\text{H}_2\text{S}$  compared to the other amine solutions. From Figure 6, it can be seen that MDEA had the best  $\text{H}_2\text{S}$  absorption performance that increases with linear profile compared with TEA and MEA. Herein, as stated above, this might have been caused by the low water content of MDEA that resulted in optimal gas absorption.

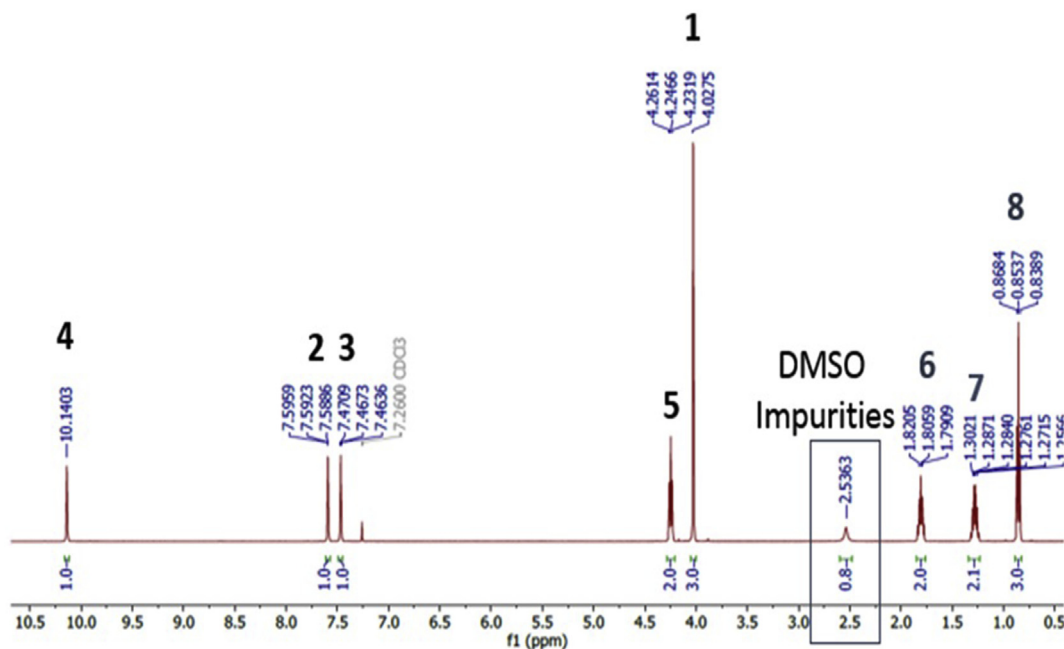


Figure 4.  $^1\text{H-NMR}$  characterization result of [bmim][Br] ionic liquid.

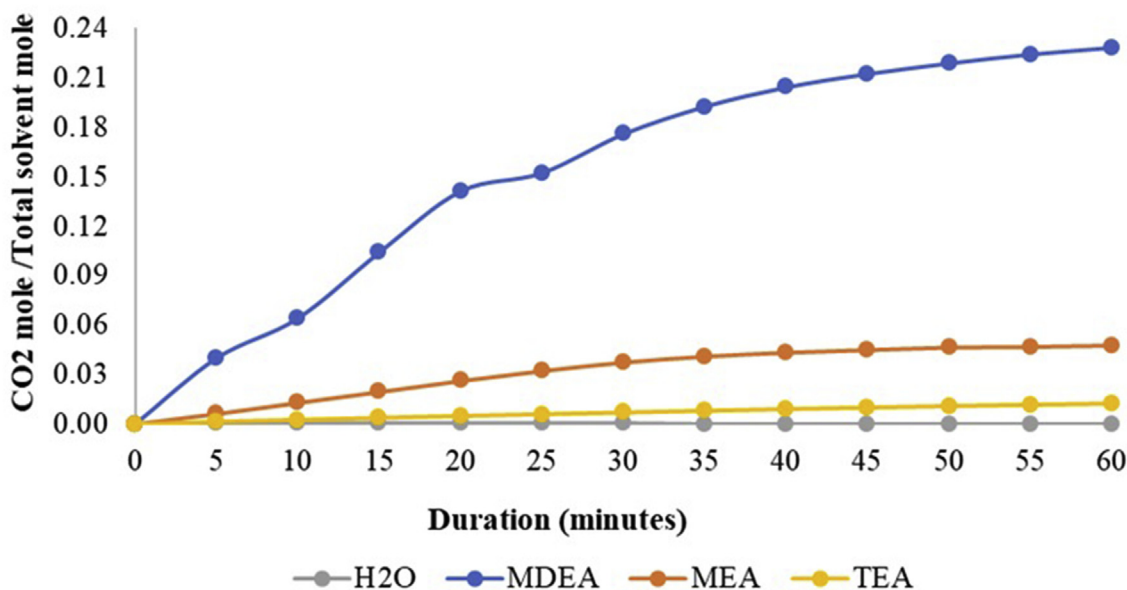


Figure 5. CO<sub>2</sub> gas absorption in water and amine solutions.

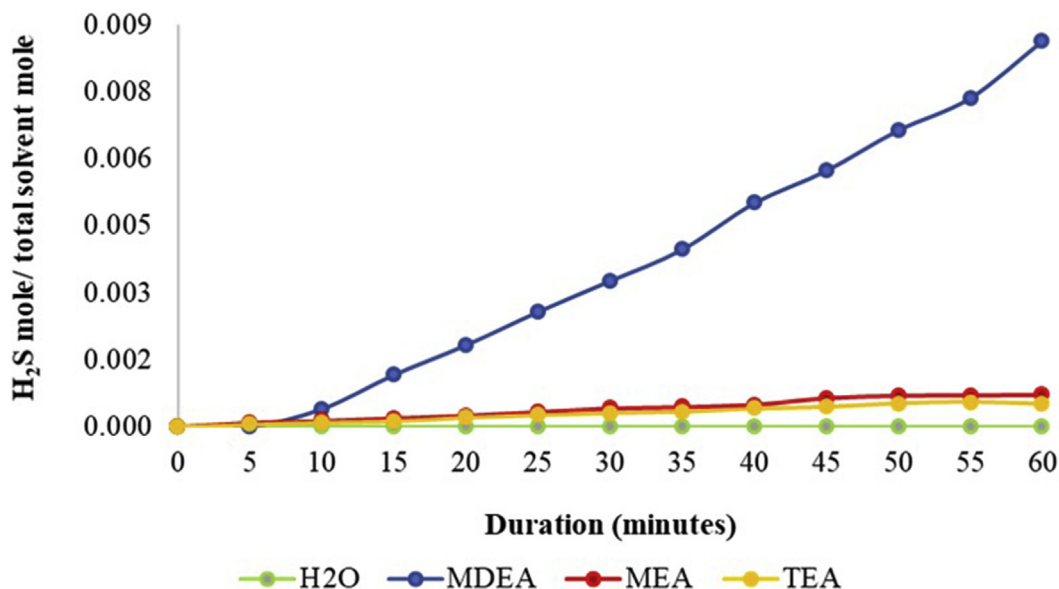


Figure 6. H<sub>2</sub>S absorption in water and amine solution.

### 3.3. Gas absorption in mixture of water and [bmim][Br] ionic liquid

Figure 7 compares the solubility of CO<sub>2</sub> in [bmim][Br] ionic liquid with the concentration of 100 wt%, 75 wt%, 50 wt%, and 25 wt% in the mixture with water. One can see that the total CO<sub>2</sub> mole absorbed in [bmim][Br] ionic liquid was increased with the decrease of water content increment in [bmim][Br], and the pure ionic liquid solution absorbed the most of CO<sub>2</sub> in 60 min of the absorption process. Even though the absorbed CO<sub>2</sub> slightly decreased at 40 min of absorption time for pure [bmim][Br] ionic liquid, the absorption did not reach the saturated point until 60 min absorption time. The same trend could also be observed in H<sub>2</sub>S absorption for the same duration as shown in Figure 8. The pure [bmim][Br] solution had the best H<sub>2</sub>S absorption performance while there was no H<sub>2</sub>S absorbed in [bmim][Br] 75 wt% and 50% wt% solutions.

As stated above, pure water had inferior performance in absorbing CO<sub>2</sub> and H<sub>2</sub>S. In the mixture with ionic liquid, water addition to [bmim]

[Br] would create bonds with anion and cation in ionic liquid to create clusters and upset the structure of the ionic liquid. Previous research found that CO<sub>2</sub> and H<sub>2</sub>S absorptions are influenced by anion and cation interaction in ionic liquids structure with the acid gas. In the mixture of ionic liquids and water, the presence of hydrogen bonds in the water structure can significantly affect the properties of ionic liquids. In addition, the bond competitions between water–water, cation–anion, and water–ionic liquids interactions in the mixture of [bmim][Br]-water hinder the interaction of the solvent with the gas. Hence, those reasons diminish the capability of mixture [bmim][Br]-water to absorb gases [15, 26]. Therefore, the pure [bmim][Br] ionic liquid was the optimum solvent to absorb CO<sub>2</sub> and H<sub>2</sub>S gas.

### 3.4. Gas absorption in mixture of [bmim][Br] ionic liquid and MDEA

Figure 9 and Figure 10 show the gas absorption results in the mixture of [bmim][Br] ionic liquid and MDEA with the mass ratio of 1:1, 1:3, and

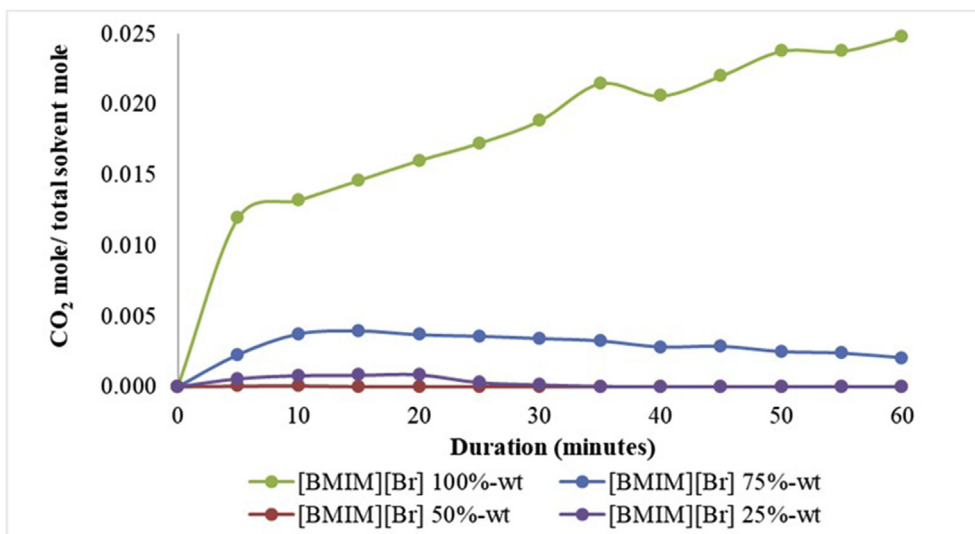


Figure 7. Solubility of CO<sub>2</sub> in [bmim][Br] ionic liquid for various concentration.

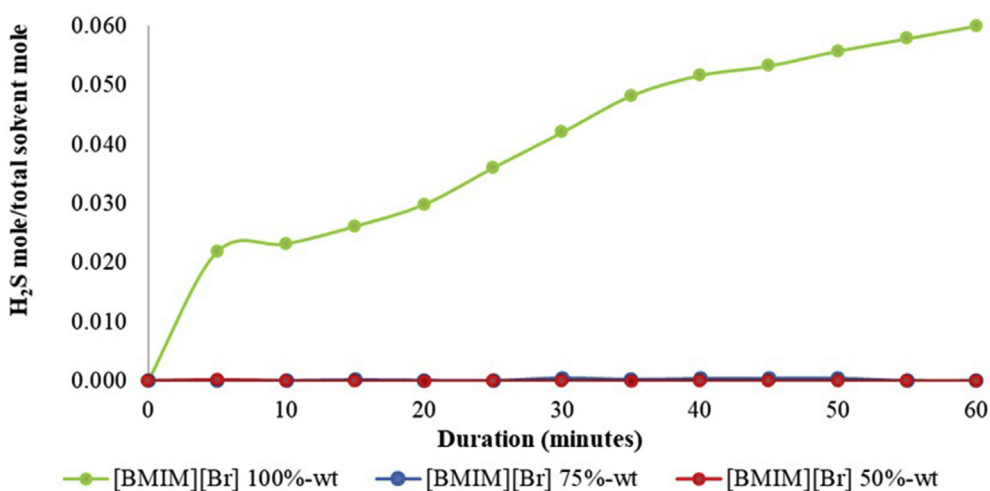


Figure 8. Solubility of H<sub>2</sub>S in [bmim][Br] ionic liquid for various concentration.

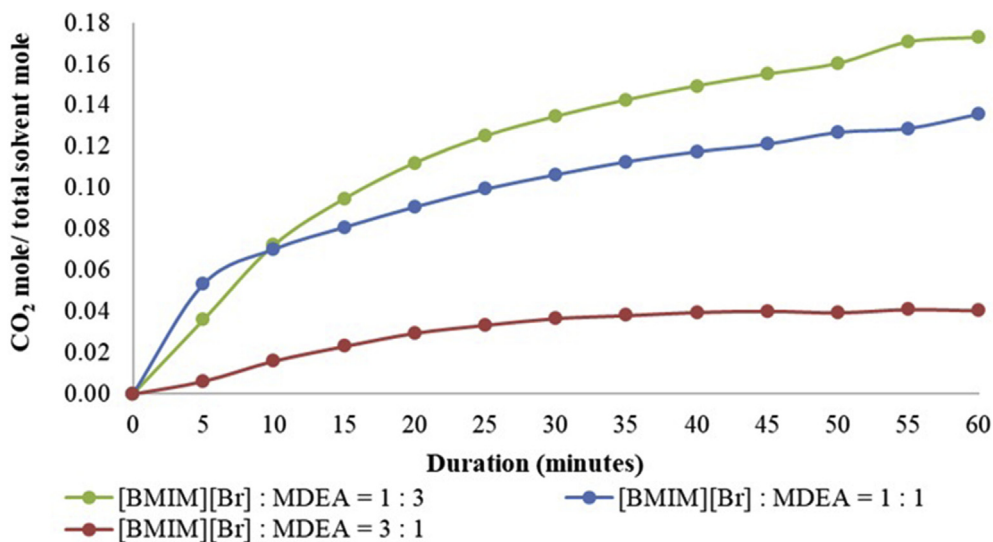


Figure 9. CO<sub>2</sub> absorption in the mixture of [bmim][Br] and MDEA.

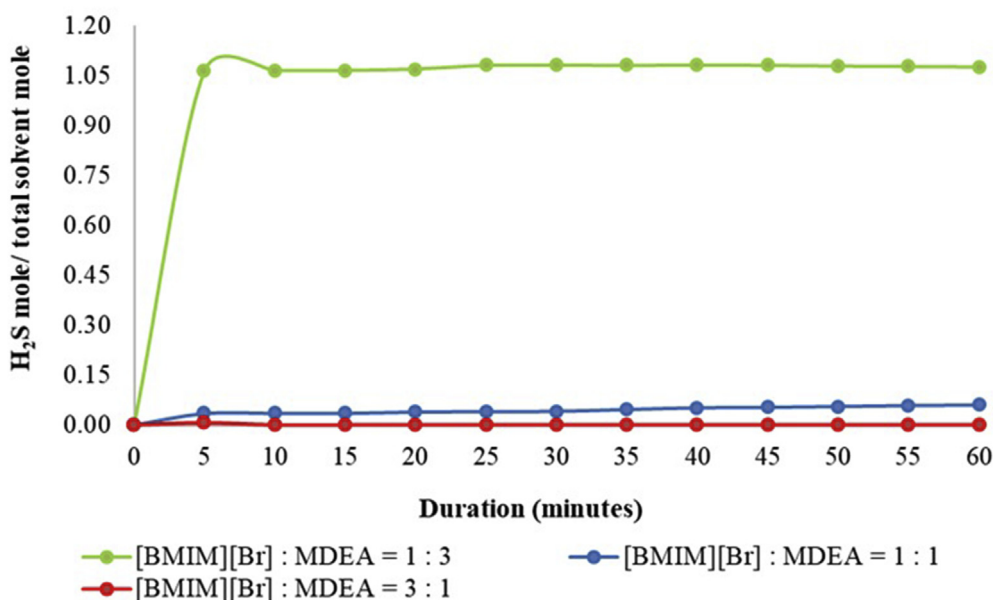


Figure 10. H<sub>2</sub>S absorption in the mixture of [bmim][Br] and MDEA.

3:1 for CO<sub>2</sub> and H<sub>2</sub>S at a constant flow rate of 6 mL/min, respectively. As shown by Figure 9, the CO<sub>2</sub> gas absorption profile by three of the mixture increased exponentially during 60 min absorption time with the mixture of [bmim][Br]-MDEA with 1:3 mass ratio has the best performance. Yu et al. [27] indicated that higher amine concentration in the mixture with ionic liquids is favorable for CO<sub>2</sub> absorption. While Figure 10 shows that the mixture of [bmim][Br]-MDEA with 1:3 mass ratio absorbed the most H<sub>2</sub>S as well compared with other mixing proportions with relatively constant absorption profiles. Haghtalab and Afsharpour [28] confirmed that high ionic liquids concentration in the mixture with amine solution leads to lower H<sub>2</sub>S absorption, especially at high temperatures. Both results show that the mixture of [bmim][Br]-MDEA with a 1:3 mass ratio absorbed more H<sub>2</sub>S than CO<sub>2</sub> during 60 min absorption time. In the CO<sub>2</sub> absorption case, the CO<sub>2</sub> absorbed in the mixture solvents increases in 60 min. However, in the H<sub>2</sub>S absorption case, the absorbed H<sub>2</sub>S reaches its saturated point at the beginning of the absorption process. Huang et al. [29] confirmed that H<sub>2</sub>S absorption has a higher rate than CO<sub>2</sub> absorption in the mixture of ionic liquids-amine solvent.

The idea of mixing ionic liquids with amine solutions provides relatively lower cost and lower partial pressures compared with the conventional acid gas removal process using amine solutions [30]. The mixture of [bmim][Br] and MDEA creates functionalized ionic liquids with a free tertiary amine group tethered on the cations of the ionic liquids. As a result, increasing MDEA amount increases free tertiary amine group base properties on the solvent mixture as a functional site for CO<sub>2</sub> and H<sub>2</sub>S absorption [29]. Hence, it enhances the solubility of CO<sub>2</sub> and H<sub>2</sub>S in the solvent mixture compared with those solvents in pure conditions.

### 3.5. H<sub>2</sub>S/CO<sub>2</sub> selectivity in various solvents

Table 2 shows H<sub>2</sub>S/CO<sub>2</sub> selectivity in MDEA, [bmim][Br], and their mixture at various proportions that only applied to CO<sub>2</sub> gas feed with 100%-v purity and H<sub>2</sub>S gas feed with 1%-v purity at ambient condition. It should be noted that the solubility of CO<sub>2</sub> and H<sub>2</sub>S in amine solutions decreases by the decrease of partial pressure and the increase of operating temperature [31]. Thus, the very low H<sub>2</sub>S/CO<sub>2</sub> feed ratio used in this research might be why commercial MDEA solution is poorly selective to H<sub>2</sub>S compared with synthesized [bmim][Br] ionic liquid at room temperature. In comparison, the high H<sub>2</sub>S/CO<sub>2</sub> selectivity by pure [bmim][Br] ionic liquid is determined by the interaction of hydrogen

Table 2. H<sub>2</sub>S/CO<sub>2</sub> selectivity at 60 min of absorption in ambient temperature and pressure.

Solvent	CO <sub>2</sub> mole/solvent mole	H <sub>2</sub> S mole/solvent mole	H <sub>2</sub> S/CO <sub>2</sub> selectivity
MDEA	0.228	0.009	0.038
[bmim][Br]	0.025	0.060	2.417
[bmim][Br]:MDEA = 1:3	0.173	1.075	6.222
[bmim][Br]:MDEA = 1:1	0.136	0.059	0.439
[bmim][Br]:MDEA = 3:1	0.040	0	0

Table 3. Comparison of H<sub>2</sub>S/CO<sub>2</sub> selectivity in this research with various reported ionic liquids.

Solvent	Temperature (K)	Pressure (kPa)	H <sub>2</sub> S/CO <sub>2</sub> selectivity	Ref.
1-butyl-3-methylimidazolium bis(2-ethylhexyl) sulfosuccinate [bmim][doc]	303.15	207.3	3.488	[18]
1-(2-Hydroxyethyl)-3-methylimidazolium Tetrafluoroborate [hemim][BF <sub>4</sub> ]	303.15	175	2.167	[32]
1-ethyl-3-methylimidazolium ethylsulfate [emim][EtSO <sub>4</sub> ]	303.15	122	1.667	[33]
1-octyl-3-methylimidazolium tetrafluoroborate [Omim][BF <sub>4</sub> ]	303.15	1021	3.052	[34]
[bmim][Br]	303.15	101.3	2.417	This work
[bmim][Br]:MDEA = 1:3	303.15	101.3	6.222	

bond in H<sub>2</sub>S with [bmim][Br] ionic liquid cation that generates stronger bonding than the interaction between CO<sub>2</sub> and the ionic liquid. The interaction between the anion atom, Br, and S atom of H<sub>2</sub>S is dominantly affected by the affinity of [bmim][Br] ionic liquid to H<sub>2</sub>S as well [15].

Table 3 summarizes and compares the reported CO<sub>2</sub> and H<sub>2</sub>S separation results using various ionic liquids as the solvent at a specific temperature and pressure [18,32,33,34]. It is suggested that pure synthesized [bmim][Br] ionic liquid had relatively good selectivity in

H<sub>2</sub>S/CO<sub>2</sub> separation compared with other pure ionic liquids. Herein, the mixture of [bmim][Br]-MDEA with a 1:3 mass ratio increased the selectivity towards H<sub>2</sub>S significantly compared to the separation performance of any other pure ionic liquids. It should be noted that hydrophobic protic ionic liquids formed by hydrophobic functionalized ionic liquids tethered with a free tertiary amine group on their cations were expected to have absorption selectivity of H<sub>2</sub>S from CO<sub>2</sub>. In addition, the reaction between CO<sub>2</sub> with tertiary amine hardly occurred, both thermodynamically and kinetically. This phenomenon is due to the absence of active protons in the CO<sub>2</sub> molecule [35]. Hence, a high amount of MDEA in the solvent mixture with [bmim][Br] prefers to absorb H<sub>2</sub>S more than CO<sub>2</sub>, even in the low H<sub>2</sub>S/CO<sub>2</sub> feed ratio.

#### 4. Conclusions

The [bmim][Br] ionic liquid was successfully synthesized in this study. Its capacity and selectivity to separate CO<sub>2</sub> and H<sub>2</sub>S from natural gas were investigated, especially for the low ratio of H<sub>2</sub>S/CO<sub>2</sub> in ambient temperature and pressure. The absorption performance results were compared with amine solutions such as MEA, TEA, and MDEA, and water as benchmarking. The acid gas absorption in the mixture of [bmim][Br] ionic liquid and MDEA at various compositions were also observed. It is found that the pure [bmim][Br] solvent was more selective to H<sub>2</sub>S rather than pure MDEA with the selectivity of 2.417 and 0.038, respectively. Comparison of H<sub>2</sub>S/CO<sub>2</sub> selectivity with some other reported ionic liquids shows that pure synthesized [bmim][Br] ionic liquid has relatively acceptable performance. In addition, the mixture of [bmim][Br]-MDEA with a 1:3 mass ratio increases the selectivity towards H<sub>2</sub>S significantly with the H<sub>2</sub>S/CO<sub>2</sub> selectivity of 6.2. The free tertiary amine group tethered in the cations of ionic liquids in the mixture became a functional site that leans to absorb more H<sub>2</sub>S. However, H<sub>2</sub>S and CO<sub>2</sub> gas absorption using [bmim][Br] and MDEA were hugely affected by water content. Thus, the water content in each solvent should be measured and minimized before operation. Even though the industrial applicability in the acid gas removal process still needs further investigation, this research proposed a promising idea for selective absorption of H<sub>2</sub>S/CO<sub>2</sub> in natural gas treatment.

#### Declarations

##### Author contribution statement

Tri Partono Adhi: Conceived and designed the experiments; Analyzed and interpreted the data.

Yohanes Andre Situmorang: Analyzed and interpreted the data; Wrote the paper.

Haryo Pandu Winoto: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data.

Danu Ariono: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Diannisa Septiana & Patricia Imanuela: Performed the experiments; Wrote the paper.

Antonius Indarto: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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##### Data availability statement

Data included in article/supp. material/referenced in article.

#### Declaration of interests statement

The authors declare no conflict of interest.

#### Additional information

No additional information is available for this paper.

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