Reducing Free Fatty Acids in Crude Palm Oil Using Diethylene Glycol and Zinc(II) Chloride Based Deep Eutectic Solvent

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Received: June 20, 2023
Accepted: February 20, 2024

DOI: 10.22146/ijc.85980

Abstract: *Deep eutectic solvents (DES) were prepared by precise combinations of mol fractions of chemical compounds, resulting in a lowered melting point due to hydrogen bonding. This research aimed to elucidate the physicochemical attributes of DES and its effectiveness in mitigating free fatty acid (FFA) levels in crude palm oil (CPO). Zinc(II) chloride ($ZnCl_2$) served as the hydrogen bond acceptor (HBA) while diethylene glycol (DEG) as the hydrogen bond donor (HBD). Characterization included freezing point, density, viscosity, conductivity, and pH determination. At a $ZnCl_2$ mol fraction of 0.30, the resulting DES exhibited homogeneity with transparent liquid properties, featuring a freezing point below −10 °C, density of 1.42 g/mL, viscosity of 1933.40 cP, conductivity of 66.13 μS/cm, and pH 3.42. FTIR spectra confirmed hydrogen bond interactions between HBA and HBD. Applied to CPO at a 1:1 volumetric ratio (DES:CPO), with 2 h of stirring time at 50 °C, FFA content decreased from 4.11 to 0.86%. This research highlights DES as an environmentally sustainable purification agent, significantly reducing FFA levels in unrefined palm oil.*

Keywords: *free fatty acids; CPO; diethylene glycol; deep eutectic solvent; hydrogen bond*

■ INTRODUCTION

Crude palm oil (CPO) is obtained from palm oil pulp through sterilization and pressing processes. CPO is widely used as raw material for the cooking oil, soap, and biodiesel industries [1-2]. CPO has great potential as a raw material for making biodiesel because of its amount of 22–40% in ripe palm oil fruit [3]. In addition, CPO price, which is cheaper than palm olein with food grade quality, can be an alternative raw material for making biodiesel [4].

A critical determinant of CPO quality is the presence of free fatty acids (FFA), which are liberated acids from triglycerides [5]. As Japir et al. [6] outlined, the maximum permissible requirement for CPO quality is 5%. Various factors influence FFA levels, including the fruit's grade at harvest, delays in fruit processing, and rough handling. CPO exceeding the 5% FFA threshold will result in a reduced selling price, necessitating FFA reduction measures [5]. Another crucial thing is that in making biodiesel, CPO with an FFA content of less than 1% is needed [7]. The meticulous selection of CPO samples with an initial FFA content of 4.11% is proximate to the industry's maximum threshold of 5%. This deliberate choice intends to represent precisely practical conditions within the palm oil processing industry.

Deep eutectic solvent (DES) is an environmentally friendly solvent that has numerous innovative uses for these solvents across diverse fields. DES has extensive applications in high-purity extraction and separation processes. Eutectic solvents have advantages over ionic liquids (ILs), which are easy to produce, inexpensive, environmentally friendly, and nonpoisonous [8]. In addition, DES has the benefit of being non-volatile and non-flammable, like organic solvents [9].

This research proposes an alternative strategy for decreasing FFA in CPO by employing deep eutectic solvents (DES) derived from zinc(II) chloride ($ZnCl_2$) as the hydrogen bond acceptor (HBA) and diethylene glycol (DEG) as the hydrogen bond donor (HBD). DEG acts as the HBD, supplying hydrogen donors to $ZnCl_2$

and facilitating hydrogen bond formation. The DEG and $ZnCl_2$ enable hydrogen bonding between the OH groups in DEG and Cl groups in $ZnCl_2$. In this research, $ZnCl_2$ is employed as the HBA because it possesses two Cl- groups, which serve as proficient hydrogen acceptors. The selection of $ZnCl_2$ is predicated on its cost-effectiveness, facile handling, and expeditious formation of DES when conjoined with other components acting as HBD [10]. Furthermore, DEG is chosen based on the presence of two OH groups, serving as hydrogen donors and its discernibly low level of toxicity [11].

The resulting DES effectively reduces FFA in palm oil by establishing hydrogen bonds between Cl^- in DES and H^+ in FFA. This research not only utilizes $ZnCl_2$ as a HBA and DEG as a HBD to reduce FFA in CPO but also environmentally friendly approaches to augment palm oil quality. The research provides valuable insights into sustainable methodologies for reducing FFA, addressing environmental concerns, and advocating eco-friendly practices within the palm oil industry. Consequently, this research aims to characterize the physicochemical properties of DES, assess FFA reduction in palm oil, and evaluate palm oil quality pre- and post-DES mixing.

■ EXPERIMENTAL SECTION

Materials

Materials of DES, such as DEG, were purchased from Merck, and $ZnCl_2$ was purchased from Pudak. CPO was obtained from PT. Pundi Lahan Khatulistiwa, West Kalimantan, Indonesia. Bleaching earth (BE) and distilled water (H_2O) were bought from the market. Materials for determining the quality of CPO such as 2-propanol (C_3H_7OH), starch ($(C_6H_{10}O_5)_n$), glacial acetic acid (CH_3COOH), hydrochloric acid (HCl), oxalic acid ($C_2H_2O_4$), phenolphthalein, potassium iodate (KIO_3), potassium iodide (KI), chloroform ($CHCl_3$), sodium hydroxide (NaOH), sodium thiosulfate pentahydrate ($Na_2S_2O_3{\cdot}5H_2O$) were also purchased from Merck.

Instrumentation

The equipment and instruments used in this work included burette, hotplate (Hotplate-IKA C-MAG HS 7), conductivity meter (PCT-407), standard laboratory glass-wares, magnetic stirrers, ovens (Memmert), Fourier transform infrared (FTIR) spectrometer (Thermo Scientific Nicolet iS10), pH meter (PCT-407), centrifuge (Oregon LC-04S), UV-visible spectrophotometer (Shimadzu UV-2600), and viscometer Ostwald (Schott Capillary-Viscometer 513 23).

Procedure

DES preparation

DES preparation refers to the research by Adhitya et al. [12] with little modification, where $ZnCl_2$ as HBA and DEG as HBD were heated at 80 °C for 1 h. Then, the eutectic mixture was prepared by adding HBD to the HBA with variations of mol fraction of $ZnCl_2$ (x_{ZnCl2}): 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, and 0.90. The eutectic mixture with a colorless homogeneous liquid at room temperature will be further analyzed.

DES characterization

The characterization of DES refers to research by Rahmalia et al. [13] and Adhitya et al. [12], where the freezing point was tested by placing DES in the freezer and measuring the freezing point of the sample using a thermometer. The density test was carried out by weighing the sample mass in a pycnometer. The viscosity test was carried out using the viscometer Ostwald. The pH test was carried out with a pH meter, where the probe on the pH meter was dipped into the test solution. Furthermore, the pH value was obtained from the measurement results. The conductivity of the eutectic solvent was analyzed using a conductivity meter. The electrode on the conductivity meter was immersed in the sample to obtain the conductivity value from the measurement results. The functional groups of the eutectic solvent before and after the addition of CPO were analyzed using FTIR.

CPO preparation

CPO preparation refers to Anis et al. [14], where the bleaching process was carried out to absorb color pigments using BE. The bleaching process was carried out by mixing 5% w/w BE from the total weight of CPO. Furthermore, the oil and BE were separated by centrifuging for 20 min at a speed of 3000 rpm at room temperature. Then, the oil was heated at 105 °C for ± 3 h.

Reducing FFA levels in CPO

FFA level reduction refers to research by Mulia et al. [15] with slight modifications, in which CPO and DES were mixed with variations of x_{ZnCl2}, variations in the ratio of DES:CPO, variations in stirring time at 50 °C and stirring at 500 rpm. The temperature during stirring was maintained at 50 °C to reduce the risk of oil damage. Separating DES and FFA was performed using a centrifuge for 30 min at 3000 rpm.

FFA levels measurement

FFA levels measurement refers to the AOCS Ca 5a-40 [16], which is carried out by adding 0.1 g of CPO to a 50 mL Erlenmeyer. Next, 3 mL of 2-propanol was added to the Erlenmeyer and heated at 40 °C until the oil dissolved. Then, five drops of phenolphthalein indicator were added to the mixture and titrated with NaOH solution until it turned pink. FFA level measurement was also carried out on treated CPO. FFA levels were determined by Eq. (1);

$$\text{FFA content} = \frac{256 \times \text{N NaOH} \times \text{V NaOH}}{\text{W} \times 10} \times 100\% \quad (1)$$

where 256 is the palmitic acid relative molecular mass (g/mol) as the major free fatty acid present in palm oil, N NaOH is the normality of titter solution (N), V NaOH is the volume of titter solution used (mL), and W is the sample weight (g).

Peroxide number measurement

The peroxide number test referred to by Cox and Pearson [17], was carried out by weighing 0.5 g of CPO and putting it in a 50 mL Erlenmeyer. Then, mix 1.5 mL of glacial acetic acid and 1 mL of chloroform into the Erlenmeyer. Next, put 0.3 mL of 20% potassium iodide into the Erlenmeyer and shake vigorously. Incubate the mixture for 30 min in a dark place at room temperature. After that, mix 5 mL of distilled water into the incubated mixture, shake vigorously, and add 3 mL of the starch indicator. Titrate the resulting mixture with 0.02 N sodium thiosulphate pentahydrate solution until the black color changes to colorless. Tests were also carried out on blanks with the same treatment. The value of the peroxide number can be determined by Eq. (2);

$$\text{Peroxide number} = \frac{(v_1 - v_0) \times N}{m} \times 1000 \quad (2)$$

where v_0 is the blank volume (mL), v_1 is the volume of titrant solution used (mL), m is CPO mass (g), and N is the normality of titter solution (N).

Water content measurement

Water content measurement referred to AOCS Ca 2c-25 [18], was carried out by heating the weighing bottle at 105 °C for 1 h and then, cooled in a desiccator for 30 min and weighed. After that, CPO was put into the weighing bottle and weighed the total mass. Then, the bottle was heated in the oven at 105 °C for 1 h. The weighing bottle containing the sample was stored in the desiccator for 30 min and weighed the mass obtained. Heating and weighing were repeated until a constant weight was obtained, and the water content in the resulting CPO was calculated. The water content in CPO was determined by Eq. (3);

$$\%\text{Water content} = \frac{m_1 - m_2}{m_1} \times 100\% \quad (3)$$

where m_1 is the mass of the weighing bottle and CPO before heating (g), and m_2 is the mass of the weighing bottle and CPO after heating (g).

RESULTS AND DISCUSSION

The Physical Characteristics of DES

Preparation and characterization of DES

DES was acquired by mixing DEG as a HBD and $ZnCl_2$ as a HBA with x_{ZnCl2} variations. The variation of x_{ZnCl2} was conducted to determine the best mixture with suitable characteristics to be used as a solvent to reduce FFA in CPO. DES was prepared by heating DEG and $ZnCl_2$ at 80 °C for 1 h to remove hydrate in DEG and water vapor that might be contained in $ZnCl_2$. DEG is hydrated, while $ZnCl_2$ is hygroscopic [1]. The water content in the manufacture of DES will disrupt the hydrogen bonds between chloride ions from $ZnCl_2$ and OH groups from DEG [19]. In addition, the water content in DES will affect the stability of the resulting DES [20]. The eutectic solvent with variations x_{ZnCl2} was presented in Fig. 1, and a description of the eutectic solvent were presented in Table 1.

Based on the results in Fig. 1 and Table 1, M1, M2, and M3 obtained clear liquids, indicating that DES were formed. Meanwhile, M4-M9 was crystallized due to $ZnCl_2$

Table 1. Forms of eutectic solvents based on $ZnCl_2$:DEG at room temperature

x_{ZnCl2}	Mixture code	Mixture form
0.10	M1	Clear, liquid
0.20	M2	Clear, liquid
0.30	M3	Clear, liquid
0.40	M4	Clear, contains solids
0.50	M5	Clear, contains solids
0.60	M6	Clear, contains solids
0.70	M7	Crystallization
0.80	M8	Crystallization
0.90	M9	Crystallization

and DEG not entirely interacting, so they could not form a clear liquid at room temperature [12,20]. The DES formed (MI, M2, and M3) were tested for their physicochemical properties to determine the characteristics of the DES. The physicochemical tests included freezing point, density, viscosity, conductivity, pH, and FTIR analysis to determine the hydrogen bonds formed between $ZnCl_2$ and DEG.

Freezing point. The initial components of DES, that is, $ZnCl_2$ and DEG, have freezing points of 290 and 6.5 °C, respectively [10,21-22]. Mixing these two components in x_{ZnCl2} can decrease the freezing point significantly. The freezing point obtained in the eutectic mixture was lower than the freezing point of its constituent components [12]. The relationship between x_{ZnCl2} and the freezing point in the form of a phase diagram is presented in Fig. 2.

Fig. 2 shows the mixed phase between $ZnCl_2$ and DEG. Based on the diagram, the eutectic points with the lowest freezing points were obtained by DES-1, DES-2, and DES-3, below −10 °C. The lowering of the freezing point experienced by the eutectic mixture can be caused by the stretching of charged ions between the hydrogen halide ion bonds and HBD [21]. According to Adhitya et al. [12], the factors affecting DES's lowering freezing point are the eutectic solvent's lattice energy, the interaction of HBA and HBD, and the change in entropy due to liquid formation.

Density. Density is a parameter that affects the extraction process due to mass transfer. $ZnCl_2$-based DES generally has a greater density than water, ranging from 1.3 to 1.6 g/cm^3 at 25 °C. The density measured in this work was DES with a clear liquid at room temperature and a lower freezing point than its constituent components. The density measurement was done by weighing the DES in a 5 mL pycnometer at room temperature. Table 2 shows

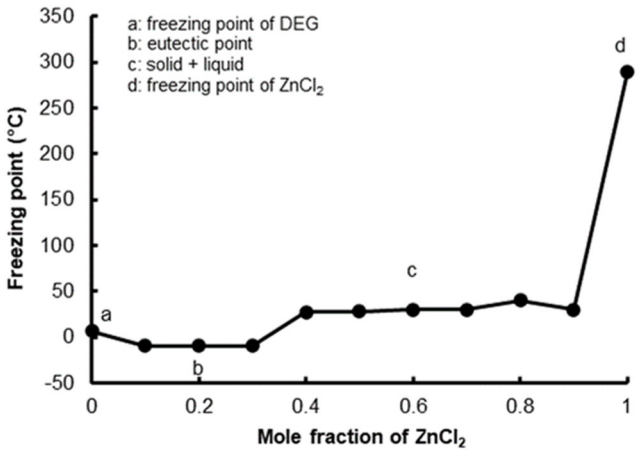

Fig 2. Eutectic phase diagram of $ZnCl_2$:DEG mixture

Fig 1. The mixture of $ZnCl_2$ and DEG

Table 2. Physicochemical of DES

DES code	x_{ZnCl2}	Density (g/mL)	Viscosity (cP)	Conductivity (μS/cm)	pH
M1	0.10	1.21	69.03	256.67	3.92
M2	0.20	1.32	222.09	167.30	3.77
M3	0.30	1.42	1933.40	66.13	3.42

that the greater x_{ZnCl2} in DES, the greater the density of DES obtained due to the contribution of the pure components composing the DES. The density of DES will increasingly lead to a high $ZnCl_2$ density as x_{ZnCl2} increases [23].

Viscosity. The DES viscosity generally has a value of > 100 cP at room temperature, which is higher than the viscosity of water. The high viscosity of DES is due to the vast hydrogen bonding interactions between components [12-13]. The low viscosity of DES is desirable because it approaches the viscosity of widely used organic solvents [23]. In this research, viscosity measurement was carried out by measuring the flow time of the eutectic solvent using an Ostwald viscometer. Based on Table 2, increasing x_{ZnCl2} will cause the viscosity of the eutectic solvent to increase. The increase in viscosity was caused by expanding hydrogen bonds between each component, so the movement of free ion species decreases [14].

Conductivity. Conductivity was related to viscosity, where the lower the conductivity, the higher the viscosity. In this research, the increase in HBA and decrease in HBD in the eutectic mixture caused the conductivity to decrease. Table 2 shows that increasing x_{ZnCl2} causes a decrease in conductivity. The decrease in conductivity was caused by an increase in viscosity, which causes the movement of free ions in the eutectic solvent to decrease [24].

pH. In general, the pH of DES was ruled by the pH constants of HBA and HBD. Table 2 shows that increasing x_{ZnCl2} causes a decrease in pH. The increase in pH was also affected by the increase in the amount of $ZnCl_2$ as an acidic salt, where the more $ZnCl_2$ in the eutectic solvent, the more acidic the pH of the mixture will be [24].

FTIR analysis results. The FTIR analysis results show a structural change in the eutectic solvent mixture, which can be identified by the difference in the FTIR spectra of each component that was not mixed. The FTIR spectrum obtained is presented in Fig. 3. Based on Fig. 3, it can be seen that there is an interaction between $ZnCl_2$ and DEG in DES. The FTIR spectrum of $ZnCl_2$ obtained produced peaks at wave numbers 3565 cm^{-1} for the stretching vibration of the O–H group, 1618 cm^{-1} for the bending vibration of the H–O–H group, and 519 cm^{-1} for the vibration of the Zn–Cl group [25]. In comparison, the DEG spectrum obtained showed a peak at 3339 cm^{-1} stretching vibration of the O–H group, 2924 cm^{-1} asymmetric stretching vibration of the CH_2 group, 2869 cm^{-1} symmetric stretching vibration of the CH_2 group, 1125 cm^{-1} stretching vibration of the COC group, and 1052 cm^{-1} asymmetric vibration of the COC group [26-28].

The FTIR spectrum of the eutectic solvent obtained tends to be similar to the DEG spectrum obtained due to the larger mass of DEG compared to the mass of $ZnCl_2$ in the eutectic solvent preparation process. The peak of the eutectic solvent spectrum appears at 3350 cm^{-1} stretching vibration of the O–H group, 2937 cm^{-1} asymmetric

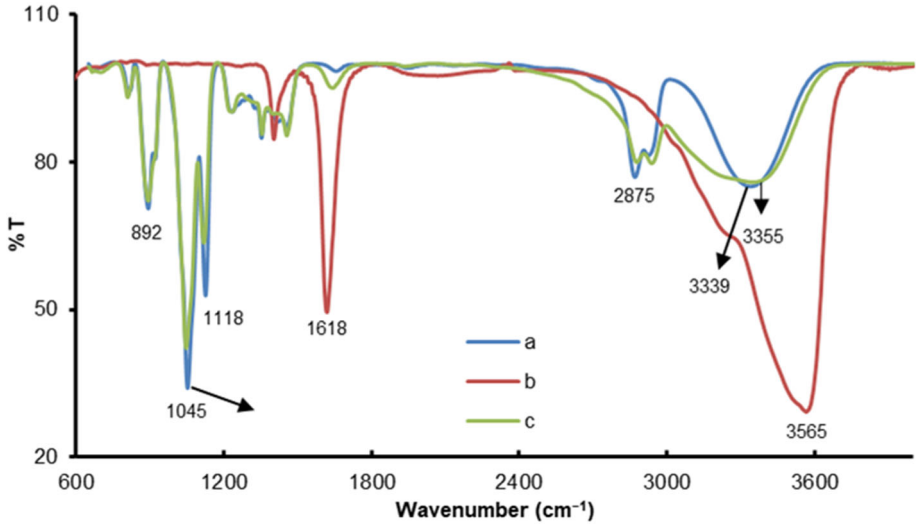

Fig 3. FTIR spectrum of (a) DEG, (b) $ZnCl_2$, and (c) DES x_{ZnCl2} 0.30

stretching vibration of the CH_2 group, 2876 cm^{-1} symmetric stretching vibration of the CH_2 group, 1118 cm^{-1} stretching vibration of the CO group, and 1046 cm^{-1} asymmetric vibration of the COC group. There was no significant difference in the FTIR spectrum of the eutectic solvent after being mixed with CPO. The peak was obtained at 3355 cm^{-1} stretching vibration of the O–H group, 2937 cm^{-1} asymmetric stretching vibration of the CH_2 group, 2875 cm^{-1} symmetric stretching vibration of the CH_2 group, 1118 cm^{-1} stretching vibration of the CO group, and 1045 cm^{-1} asymmetric vibration of the COC group [26-28].

The wavenumber is a value that indicates the amount of radiation frequency obtained from the frequency division by the speed of light. The low wavenumber obtained was due to the heavier atomic masses influenced by an increase in the concentration of $ZnCl_2$. It is based on Hooke's Law, which states that weaker bonds and heavier atoms create lower frequencies. Increasing the strength of the bond will cause the bond stretching energy to increase, and this will cause the wavenumber to shift in a more significant direction [29]. The interaction in DES is the formation of hydrogen bonds between $ZnCl_2$ and DEG caused by the attraction between the electronegative groups (Cl^-) in $ZnCl_2$ and hydrogen groups (H^+) in DEG. The interaction of the hydrogen bonding between $ZnCl_2$ and DEG is presented in Fig. 4.

Reduction of FFA Levels and Characterization of CPO Using DES

CPO was heated in an oven at 105 °C to minimize the water content in the oil. The bleaching process was carried out to reduce the levels of β-carotene in the oil and reduce unwanted impurities. The color of CPO was related to the carotene content in it. The redder the color of CPO, the higher the carotene content. The initial CPO sample has a deep red color, indicating high carotene levels, which will interfere with the titration process. The color of CPO decreased due to the adsorption of carotene compounds by BE [14].

FFA levels in CPO were reduced by mixing DES and CPO at a stirring temperature of 50 °C. This method decreases the potential loss of other components in the oil and causes low energy consumption because it uses relatively low temperatures at atmospheric pressure. Reducing the FFA levels in CPO was carried out by mixing CPO and the DES to form interactions of hydrogen bonds between the H^+ from (OH^-) in FFA and Cl^- from DES [15]. In this case, the DES acts as HBA, and FFA in CPO acts as HBD.

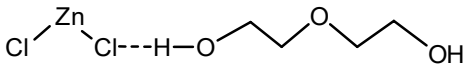

Fig 4. Estimated hydrogen bond between $ZnCl_2$ and DEG

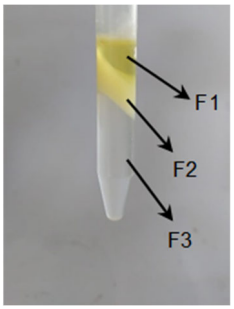

Fig 5. The phase of separated CPO& DES mixture

The mixture that was obtained was separated using a centrifuge, where the centrifuge principle was based on the density difference of the mixed compounds, namely CPO and DES. DES and the oil phase were separated into 3 phases, namely the upper phase (F1), the middle phase (F2), and the lower phase (F3). F1 was an FFA-decreased oil with a clear yellow physical appearance. F2 was a layer in the form of a gel indicated as gum from CPO, where the gum has the form of gum and mucus consisting of phospholipids, proteins, residues, and carbohydrates [30]. Meanwhile, F3 was DES. DES and oil phases were separated as lower and upper phases, respectively, due to the differences in their density [15]. The phase is shown in Fig. 5.

FFA levels were reduced in CPO by mixing CPO and DES with variations of x_{ZnCl2}, the ratio between CPO and DES, and variations in mixing time. The variation in the method was done to obtain the best conditions for the lowest FFA levels. The results of reducing FFA levels by DES with variations of x_{ZnCl2} are presented in Fig. 6. At this stage, the DES used are M1, M2, and M3. The DES:CPO volume ratio and stirring time used were 1:1

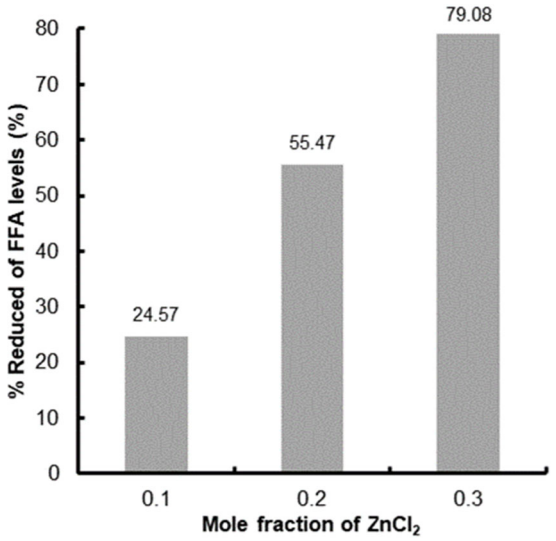

Fig 6. Reduced ALB levels in the x_{ZnCl2} variation

and 2 h, respectively. M3 obtained the best reduction of FFA due to the interaction between the hydroxyl groups in FFA and DES. According to Shahbaz et al. [31], eutectic solvents can reduce ALB due to the formation of hydrogen bonds between eutectic solvents and compounds that have hydroxyl groups (OH^-). These data indicate that viscosity is not the main determinant of the ease of interaction between DES and FFA. Increasing the mol fraction of $ZnCl_2$ causes an increase in DES molecules that have hydrogen bonds, thus allowing more hydrogen bonds to occur between DES and FFA.

Variations in DES and CPO volume ratios were carried out at volume ratios of 2:1, 2:2, 2:4, 2:8, and 2:16. The results of reducing FFA levels obtained from this variation are presented in Fig. 7. Based on Fig. 7, it can be seen that increasing the DES volume will increase the %reduction in FFA levels. The greater the volume ratio of DES will increase the possibility of hydrogen bonding between DES and FFA in CPO. It will cause a decrease in FFA [15]. When the volume ratio of DES:CPO is 2:2, the reduction in FFA levels shows the best results. This is because there is quite a large amount of DES that can interact with FFA in CPO. Furthermore, the use of DES:CPO volume ratios of 2:4, 2:8, and 2:16 reduces the amount of FFA that can interact with DES because at large volumes, while the number of DES remains constant, the distance between DES and FFA is greater [32].

Stirring time also influences the process of reducing FFA levels from CPO. The results obtained from the variations in stirring time of 15 min, 30 min, 1 h, 2 h, and 3 h were presented in Fig. 8. Based on the results obtained in Fig. 8, a stirring time of 2 h was the best because the long mixing time was very influential in reducing FFA levels in CPO. The longer the stirring process, the lower the FFA levels in CPO, which indicates that FFA in CPO was bound to the DES [33]. According to Effensi et al. [34], a stirring time of 2 h was

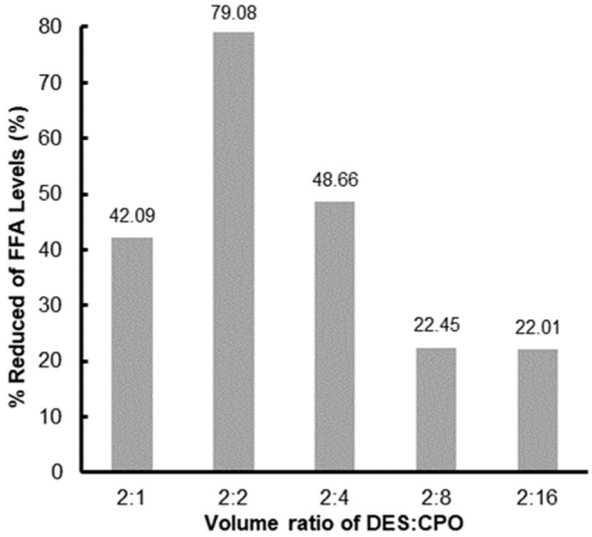

Fig 7. Reduced levels of FFA at various volume ratios of DES and CPO

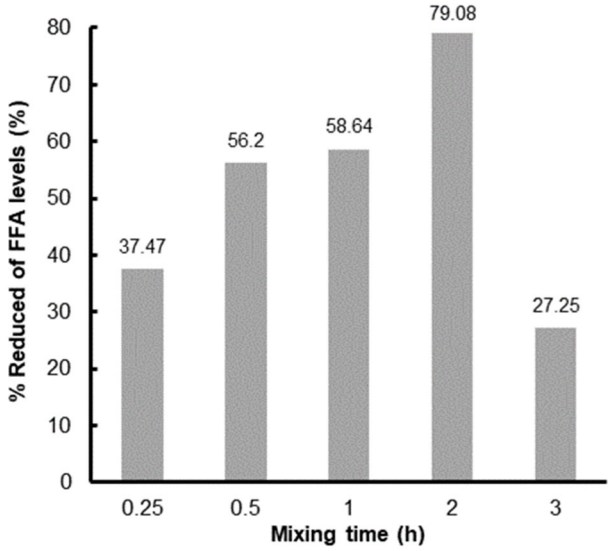

Fig 8. Reduced levels of ALB at various stirring times

the best %reduction in FFA, from 8.32 to 0.55%. However, a stirring time that is too long, namely 3 h, will reduce the effectiveness of reducing FFA levels. It was caused by the FFA conversion, which will be more significant with increasing stirring time between DES and CPO [35].

Previous research on reducing FFA in CPO using DES has been carried out by Mulia et al. [15]. DES was produced from a mixture of betaine and 1,2-butanediol, which has an extraction yield of 60%. In addition, another research reported by Putri et al. [36] that choline chloride (ChCl) and ethylene glycol (EG) as components to form DES succeeded in reducing FFA levels in used cooking oil from 7.94% to 1.28%. Hayyan et al. [20] have also carried out research related to mixing *p*-toluene sulphonic acid (PTSA) and methyl triphenyl phosphonium bromide (MTPB) and succeeded in reducing ALB levels in CPO from 9.61 to < 1%. This research shows better results than previous research, where almost 80% of FFA levels in CPO have been successfully reduced using DES based on $ZnCl_2$ and DEG.

CPO Quality Measurement

The parameters that determine the quality of CPO are FFA levels, peroxide number, and water content. The quality test aims to determine whether there is a decrease in the quality of CPO before and after treatment by DES. FFA are released when fat hydrolysis occurs. High FFA levels decrease CPO quality [1]. Titration is a method to determine FFA levels. Based on what has been obtained, it can be seen that DES can reduce FFA levels in CPO by forming hydrogen bonds between Cl^- ions in DES and OH in FFA. In addition, the bleaching process can reduce FFA levels. It follows research conducted by Ifa et al. [37], where adding bleaching earth can adsorb FFA. Although the type of FFA in CPO both before and after treatment with DES is not determined, based on literature, it has been proven that the highest fat content in CPO is palmitic acid, so the titration method used in this study calculates the total FFA in the form of palmitic acid [15,38].

The peroxide value indicates the large amount of oil that has been oxidized, where the peroxide number is used as a parameter to identify the oxidation level in the oil [39]. The peroxide number in CPO before mixing with DES was 13.78 mg ek/kg, while in CPO, after mixing with DES was 13.05 mg ek/kg. Water content is a parameter that has a role in oil hydrolysis and oxidation, which can affect the FFA levels in CPO. The high water content contained in CPO will accelerate the hydrolysis reaction into FFA and glycerol. According to Japir et al. [6], higher water content increases endogenous lipase activity, resulting in changes in the oil quality. The water content in CPO can be determined by the gravimetric method. According to AOCS Ca 2c-25 [18], the maximum water content in CPO is 0.5%. The water content obtained in CPO before mixing with DES was 0.0073%. Meanwhile, the water content in CPO after being mixed with the DES was 0.0015%.

■ CONCLUSION

DES is an alternative solvent that can be formed because of hydrogen bonding between DEG and $ZnCl_2$, so it has a lower freezing point than its constituent. Their physical properties and phase behavior depend upon the mol fraction of $ZnCl_2$, as evidenced by the formed mixture. The physicochemical properties of DES indicate that DES-based DEG and $ZnCl_2$ can be used as solvents to reduce FFA levels in CPO caused by hydrogen bonding between Cl^- in DES and H^+ in FFA. The highest reduction in FFA levels was 79.08% with a variation of x_{ZnCl2} 0.3, DES: CPO (1:1) ratio, and 2 h of stirring time. For further studies, it is also necessary to consider reducing FFA levels in CPO using DES with other materials.

■ ACKNOWLEDGMENTS

We thank Dr. Gusrizal, S.Si., M.Si. and Dr. Anthoni B. Aritonang, S.Si., M.Si. (Tanjungpura University) for helpful discussions.

■ CONFLICT OF INTEREST

The authors declare no conflict of interest.

■ AUTHOR CONTRIBUTIONS

Lieli Suryanti: conceptualization, methodology, formal analysis, and writing-original draft. Thamrin Usman and Winda Rahmalia: supervision, resources, project administration, writing-review, editing, and validation. All authors have read and agreed to the published version of the manuscript.

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