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REMOVAL OF GLYCEROL FROM PALM OIL-BASED BIODIESEL USING NEW IONIC LIQUIDS ANALOGUES

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Abstract

Upon the completion of the transesterification reaction, the produced biodiesel has to be purified from the by-product glycerol before being employed as a potential diesel substitute. The glycerol content must meet the limit set by the international biodiesel standards; namely EN 14214 and ASTM D6751. The conventional purification methods such as water washing, dry washing and membrane separation are prone to significant product loss, environmental pollution and increased production cost. In this work, seven new ternary deep eutectic solvents (DESs) were synthesised from choline chloride (ChCl) salt and two glycols-based hydrogen bond donors, namely glycerol and ethylene glycol. These DESs were employed as extraction solvents to remove total glycerol from palm oil-based biodiesel. The results revealed that the synthesised DESs have a higher total glycerol removal efficiency than that of free glycerol. Complete removal of free and total glycerol was attained by DES 3 at a molar ratio of 0.5:1 (DES 3: biodiesel).

Keywords: Eutectic, Biodiesel, Glycerol, Removal, Palm Oil, ethylene glycol.

1. Introduction

Depletion of fossil fuels due to unconstrained industrialization using non-renewable resources resamples a serious source of the current energy crisis. Hence, the potential of using biodiesel as an alternative fuel to petro-diesel is growing progressively. Biodiesel has many benefits as being biodegradable,

Abbreviations

ChCl	Choline chloride
DES	Deep eutectic solvent
DG	Diglycerides
DSC	Differential Scanning Calorimeter
FAAE	Fatty acids alkyl esters
FFA	Free fatty acid
FID	Flame ionisation detector
GC	Gas chromatography
IL	Ionic liquid
KOH	Potassium hydroxide
MG	Monoglycerides
MTPB	Methyl triphenyl phosphunium bromide
R^2	Linear correlation coefficient
RBD	Refined, bleached, deodorised
TG	Triglycerides

high cetane number and flash point (comparable to petro-diesel), low carbon exhaust gas emission and high combustion efficiency [1].

Conventionally, biodiesel can be synthesized via four techniques; viz. direct-use or blending of oils, microemulsion, thermal cracking and transesterification [2]. The most commonly practiced method is the alkali transesterification between triglyceride and alcohol to produce biodiesel known as fatty acid alkyl esters (FAAE) and by-product glycerol as shown in Scheme. 1. Alkali-catalysed transesterification takes place in three consecutive steps where the triglycerides (TGs) are initially converted to diglycerides (DGs); then conversion of DGs to monoglycerides (MGs) and lastly to glycerol as a by-product [2, 3]. Free glycerol is the remaining glycerol presents in biodiesel after separation while bound glycerol or glycerides refer to MGs, DGs, and TGs. Total glycerol is the sum of free glycerol and bound glycerol. Methanol and potassium hydroxide (KOH) are used commonly due to their high conversion of 98% within short reaction time [4].

$$\begin{array}{l} CH_2OOCR_1 \\ | \\ CH\ OOCR_2 \\ | \\ CH_2OOCR_3 \end{array} + 3R'OH \xleftrightarrow[Catalyst]{Acid\ /\ alkali} \begin{array}{l} R_1COOR' \\ R_2COOR' \\ R_3COOR' \end{array} + \begin{array}{l} CH_2OH \\ | \\ CH\ OH \\ | \\ CH_2OH \end{array}$$

Scheme. 1. The biodiesel transesterification reaction.

Despite the interesting advantages exhibited by biodiesel, it cannot substitute the conventional diesel fuel completely due to the costly and complicated biodiesel purification processes involved in its production process [4-6].

According to Atadashi, et al. [7], the downstream processing contributes 60-80% of the process cost that subsequently increases the biodiesel price. At the end of transesterification, the produced biodiesel phase is separated easily from rich glycerol phase through centrifugation or gravity settling due to the low solubility of glycerol in biodiesel phase [8]. However, the produced biodiesel phase still contains trace amount of glycerol that need to be purified to meet the

specifications set by EN 14214 and ASTM D6751 biodiesel standards. The high viscosity glycerol in biodiesel may leads to choked fuel systems, injector fouling and upsets engine's performance [5, 9]. Besides, the presence of glycerol in biodiesel also leads to the emission of harmful acrolein into the environment [10].

The most commercially available biodiesel purification methods are water washing, dry washing and membrane extraction [6, 10]. Water washing produces a significant amount of wastewater and leads to environmental problems. To efficiently purify 1L (or 1 g) of biodiesel from impurities, about 10 L (or 3 to 5g) of wastewater are generated [11]. Furthermore, more water will be required shall there is formation of emulsion due to saponification when feedstock contains high free fatty acid (FFA) [10, 12]. On the other hand, dry washing replaces water with solid chemicals such as ion exchange and magnesium silicate powder based on adsorption [10, 12]. Dry washing eradicates major problems outlined from water washing but none of the test results can satisfy the specifications mentioned in EN 14214 [10]. Lastly, the membrane technology has few benefits such as simplicity, dry, environmental friendly and reduced product loss [13-15]. Despite this, membrane separation increases the final production cost due to the expensive raw material and takes comparatively longer processing time which lags the whole production [3, 13].

Recently, ionic liquids (ILs) have gained lot attentions among researchers due to their unique characteristics in many applications as green solvents [16, 17]. However, "greenness" of the ILs is unjustified as they possess some drawbacks such as expensive raw materials, complicated preparation and purification operations and high toxicity [5, 16, 18]. In 2004, deep eutectic solvents (DESs) were reported by Abbott, et al. [19] using quaternary ammonium salts and carboxylic acids as alternatives to ILs. DESs are also known as ionic liquid analogues because they resemble various unique characteristics of ILs such as low volatility, flammability and toxicity. A DES is a mixture of two or more inexpensive and benign components (usually quaternary ammonium or phosphunium salts and hydrogen bond donors, HBD) that are associated by hydrogen bonds to form eutectic mixtures at certain molar ratio [1, 20, 21]. The resulted DESs will have freezing point lower than its constituting components at the eutectic point. This freezing point depression is due to the extensive hydrogen bonding between hydrogen bond donors and the salt anion [19, 22]. In contrast to ILs, DESs can be prepared easily using affordable raw materials [23]. Besides, DESs can be tailored for specific applications by carefully selecting the type of salt and hydrogen bond donors, and most importantly they are environmental benign. Hence, many researches have explored the applicability of these liquids as solvents for liquid-liquid extraction applications.

To begin with, It has been shown that binary DES synthesized using choline chloride (ChCl) salt and ethylene glycol as a hydrogen bond donor was able to remove all free glycerol from biodiesel due to their high polarity and presence of hydroxyl group in the DES [24]. Further exploration also revealed that ChCl: glycerol DES has the advantage of eliminating residual KOH catalyst from palm oil-based biodiesel. Besides, they also observed that new binary DESs synthesized from ChCl: ethylene glycol showed high glycerol removal (0.048wt%) compared to conventional ChCl: glycerol DES (0.031wt%) [25]. However, the possibility of using both HBDs in a ternary DES has not been investigated as a possible solvent for glycerol removal from biodiesel.

In this study, ChCl was chosen as a salt and glycerol and ethylene glycol were chosen as HBDss, from which a series of new ternary DESs were synthesized as extraction solvent to eliminate free glycerol and total glycerol from palm oil-based biodiesel to meet the biodiesel international specifications; EN 14214 and ASTM D6751 which are 0.02 wt % and 0.24 wt % respectively [5]. In this project, the removal efficiencies of free glycerol, glycerides and total glycerol using different molar ratio of DESs and biodiesel were also investigated.

2. Methodology

2.1. Materials

Palm oil (Yee Lee Sdn Bhd) was purchased from a local mart. D6584 kit contains calibration standard solutions (monoolein, diolein, triolein, glycerol, butanetriol) and two internal standard solutions (butanetriol and tricaprin) were purchased from Agilent Technologies, Malaysia. The derivation agent, *n*-methyl-*n*-(trimethylsilyl)trifluoroacetamide (MSTFA) was also purchased from the same company. Choline chloride ($C_5H_{14}CINO$), glycerol ($C_3H_8O_3$) and ethylene glycol ($C_2H_6O_2$) with high purity ($\geq$ 99%) obtained from Merck, Malaysia were used for the synthesis of DESs without further purification. Methanol (99.8%), n-heptane [gas chromatography (GC) grade] and KOH pellet were also supplied from Merck, Malaysia. Mass fraction of water in these chemicals was kept below 10^{-4} for all chemicals used.

2.2. Transesterification reaction

The basic-catalysed transesterification method was employed in this experiment to produce biodiesel. 500 g of Refined, Bleached and Deodorised (RBD) palm oil was transferred into a beaker warmed by water bath (Daniel DNP 9051) at 60 ^{O}C. Excess methanol (molar ratio of methanol: palm oil 10:1) was prepared in this experiment to shift the equilibrium for higher yield of FAAE [8, 24]. KOH as catalyst (1 wt% of palm oil) was dissolved in methanol to prepare homogenous potassium methoxide and transferred to the RBD palm oil to initiate the transesterification process. The mixture was stirred at a constant speed of 600 rpm for two hours. When the reaction was completed, the mixture was cooled to ambient temperature before transferring to a separation funnel. After overnight settling, two layers comprising an upper layer (biodiesel phase) and a lower layer (glycerol phase) were formed.

2.3. DESs synthesis

In this work, quaternary ammonium salt, namely choline chloride (ChCl) and two different hydrogen bond donors, specifically glycerol and ethylene glycol were selected to produce seven ternary DESs of different compositions. Table 1 presents the composition of different DESs and its abbreviation.

20 g of ChCl was prepared for each DES synthesis process and the masses of hydrogen bond donors were varied according to the specified molar ratios. The mass of chemicals was weighed accurately using Shimadzu TX423L (0.6 % error). The DESs were synthesised in tight and humidity-safe screw-capped bottles to prevent any contamination with atmospheric moisture [26, 27]. For a

particular composition, the prepared mixture was then heated on hot plate stirrer (IKA C-MAG HS 7) at 80 ^{O}C and 300 rpm for one hour until a homogeneous colorless liquid appeared [24, 26, 28]. The freezing points of synthesized DESs were measured using Mettler Toledo Differential Scanning Calorimeter (DSC 1 STAR^{e} system) . The DSC was calibrated against known standards (water and 2-propanol) to ensure the measurement accuracy [8, 29]. Besides, Karl Fisher titration was used to determine the water content of the synthesized DESs and the accuracy of Karl Fisher coulometer was verified with Hydranal-water standard 1.00 mg/g [27].

Table 1. Compositions of the DESs used in this work.

Abbreviation	*Molar ratio*		
	ChCl	*Glycerol*	*Ethylene glycol*
DES 1	1	1	1
DES 2	1	2	1
DES 3	1	1	2
DES 4	1	2	2
DES 5	2	1	1
DES 6	2	2	1
DES 7	2	1	2

2.4. The glycerol removal extraction process

Produced biodiesel phase was firstly separated from the lower glycerol phase. Then, the synthesised DES was added to the biodiesel phase separately at four DES: biodiesel molar ratios (0.5: 1, 1: 1, 2: 1 and 2.5: 1). The vials were then swirled at 200 rpm using an orbital shaker at ambient temperature for two hours. After two hours settling, the top layer (purified biodiesel) was separated and analysed by GC. The summarised concept for glycerol extraction of palm oil-based biodiesel using DESs is represented schematically in Fig. 1 [9, 30].

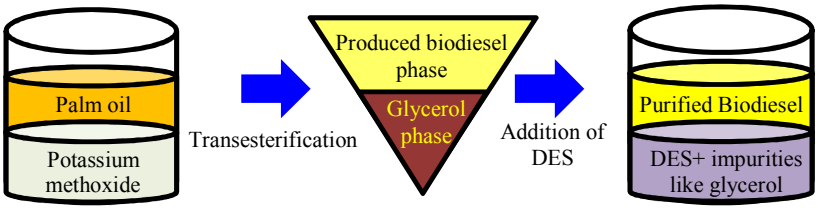

Fig. 1. Extraction of glycerol from palm oil-based biodiesel using DESs.

2.5. Chemical analysis method

The glycerol and glycerides contents in biodiesel were measured before and after extraction using DESs in accordance with analytical methods from EN 14105 and ASTM D6584-07. It was analysed using HP 6890N GC equipped with cool-on-

inlet, capillary Flame Ionisation Detector (FID) with electronic pneumatic control (EPC), analytical column DB-5ht (15 m × 0.32 mm × 0.1 µm film) and a 530 µm inner diameter high-temperature retention gap. To perform the chromatographic analysis, the prepared samples were injected by a cool-on-inlet injector at an oven temperature of 50 ^{o}C for one minute and then heated up to 180 ^{o}C at 15 ^{o}C/min rate, then the temperatures were raised to 230 ^{o}C and 380 ^{o}C at 7 ^{o}C/min and 30 ^{o}C/min rates, respectively. A front detector was kept at a temperature of 380 ^{o}C and helium was utilised as the carrier gas. Four calibration curves for free glycerol, MG, DG and TG were obtained by injecting the mixture of standard solutions at five different concentrations. The peaks of each component were identified using the relative retention time (RTT) from the internal standards. All four linear correlation coefficients (R^2) are greater than 0.95 indicated excellent linearity. The total glycerol (wt %) was then calculated as the sum of the free glycerol and bound glycerol as shown in Eq. (1) [31].

$$Total\ \ glycerol = G + 0.25MG + 0.146DG + 0.103TG \quad (1)$$

3. Results and Discussion

3.1. Synthesized DESs

During the synthesis stage, DES mixture was formed as a white viscous gel within the first 20 minutes. After 30 minutes of mixing, a liquid phase started to appear with some sediment. Mixing for an hour was required in order to obtain a homogeneous liquid phase DES.

All newly synthesised ternary DESs appeared as colourless liquids at room temperature except for DES 5. The DES 5 appeared either as a turbid white liquid or a mixture of colourless liquid and solid depending on the mixture temperature. The presence of solid particles in the mixture indicates that the amount of salt is in excess to the corresponding hydrogen bond donors (two moles of salt to one mole of glycerol and ethylene glycol). This signifies that the salt amount was in excess of that needed for forming a homogeneous DES.

In can be concluded that as the amount of HBDs increases, stronger hydrogen bonding between the DES components are formed and thus complete dissolution is observed. The unsuccessful DES 5 was not investigated further as it is not desirable as extraction solvent at room temperature.

3.2. Freezing point and water content of synthesised DESs

As clearly indicated in Table 2, all the studied DESs conform to the general behaviour of DESs as they have lower freezing points as compared to their constituting components and appear as clear liquids at ambient temperature. Besides, it can be observed that the structure of the HBD plays an important role in the extent of freezing point depression as it decreases the lattice energy and strengthen the hydrogen bonding interactions. This is proven as the freezing point decreases significantly when the molar ratio of hydrogen bond donors increases. DES 4 has the lowest freezing point which can potentially be the most valuable extraction solvent. In addition, using DES 4 can increase the amount of impurities that can be extracted without causing the freezing point of the DES to increase above the process

temperature. On the contrary, DES 7 has the highest freezing point of 22.77 ^{o}C which led to the formation of small solid sediment when it was cooled below the ambient temperature. Hence, DES 7 is suitable for industrial process where the operating temperature is slightly above the ambient temperature.

The water content of all studied DESs slightly exceeds 0.1 wt%, except for DES 1 and DES 6 as shown in Table 2. The average water content is 0.1 wt%, which is consistent with the physical properties of DESs (1 wt%). This is because the chemicals used for DESs synthesis are very hygroscopic and they readily attract water from the surroundings through sorption. In fact, the water content does not affect the extraction capability on biodiesel impurities. This is proven as some natural deep eutectic solvent (1,2-propanediol-choline chloride-water) was synthesised using water as a hydrogen bond donor to enhance its physical properties like viscosity, extractability and solubility [21]. Besides, most of the DESs do not react with water to form new components that affect extraction process [24].

Table 2. Freezing point and water content of the studied DESs.

DES	*Freezing point (^{o}C)*	*Water content (mg/kg)*
DES 1	8.36	908
DES 2	-4.28	1018
DES 3	-18.06	1158
DES 4	-23.75	1303
DES 6	12.25	959
DES 7	22.77	1189

3.3. Removal of free glycerol

The free glycerol content in biodiesel before extraction is 0.1422 wt%, which is higher than the maximum concentrations specified by the EN 14214 and ASTM D6751 (0.02 mol% and 0.02 wt% respectively). Fig. 2 and Fig. 3 demonstrate the content of free glycerol after extraction using all studied DESs. All DESs were able to reduce the free glycerol content to zero at low DES: biodiesel molar ratio (0.5:1) except for DES 6 and DES 7. When DES: biodiesel molar ratio was increased up to 2.5, all DESs (except for DES 3 and DES 7) showed poor free glycerol extraction. For DES 6, all ratios of DES: biodiesel could not meet the ASTM D6751. The maximum free glycerol removal efficiency of 100 % was achieved by all DESs at all tested DES: biodiesel molar ratios except for DES 6. The optimum glycerol removal is attained by DES 3 which eliminated all free glycerol content at the lowest DES: biodiesel molar ratio of 0.5:1.

One of the factors that affects the extraction efficiency is the DES composition molar ratio (ChCl: glycerol: ethylene glycol). As the mole fraction of ethylene glycol in DES increases from 0.33 to 0.50 (DES 1 and DES 3 in Fig. 3), the free glycerol removal efficiency increases. However, the free glycerol removal efficiency decreases when the mole fraction of glycerol in DES increases from 0.25 to 0.40 (DES 7 and DES 6 in Fig. 4). This phenomenon is well supported by research work done by Shahbaz, et al. [26] where ethylene glycol-based DESs have a bigger impact on the glycerol removal. In this work, the average free glycerol removal using the new DESs is 75.32 %.

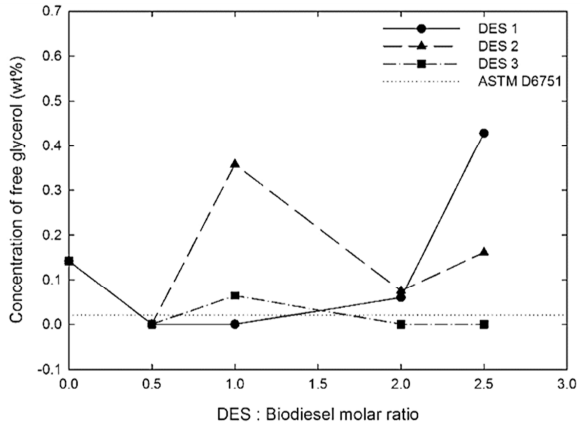

Fig. 2. Free glycerol removed by DESs (DES 1, DES 2 and DES 3).

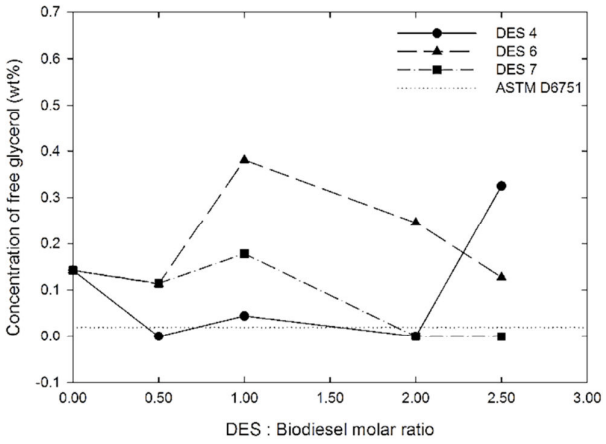

Fig. 3. Free glycerol removed by DESs (DES 4, DES 6 and DES 7).

As compared to the previous reported results performed using ammonium based DESs synthesised from ChCl as salt and ethylene glycol as hydrogen bond donors, the binary DESs were able to remove all free glycerol content (i.e. 100 % removal efficiency) at all tested DES: biodiesel molar ratio [26]. In comparison to the methyl triphenyl phosphunium bromide (MTPB) based DESs, 100 % free glycerol removal efficiency was achieved by MTPB: ethylene glycol DES at all DES: biodiesel molar ratio. However, only DES 1 from MTPB: glycerol based DESs was successful in removing free glycerol in accordance with the ASTM standard [8].

3.4. Removal of glycerides

The contents of MGs and TGs before extraction were 0.62 wt% and 0.33 wt%, respectively, which were in compliance with the EN 14214 standards (0.8 wt%

and 0.62 wt%, respectively). However, the DGs amount before extraction was 4.06 wt%, which was notably higher than the concentration limit of 0.45 wt%.

As indicated by Table 3, all DESs were able to reduce the MGs below the required concentration except for DES 4 and DES 6 at molar ratios of DES: biodiesel of 1:1 and 2:1 respectively. DES 6 and DES 7 demonstrated 100 % MGs removal efficiency at all DES: biodiesel molar ratio except for 2:1 and 1:1 respectively. In terms of optimum MGs removal, DES 2, DES 3, DES 6 and DES 7 were able to remove all MGs at minimum DES usage. The experimental DESs exhibited an average MG removal efficiency of 82.44 % which is notably higher by 10 % than that obtained by the previously reported MTPB: glycerol DES [8].

All DESs had reduced DGs to below the EN standard except for DES 1 at the molar ratio of DES: biodiesel of 2:1 and 2.5:1 as shown in Table 3. The maximum DGs removal was 100 % achieved by DES 3, DES 4, and DES 7 at the lowest DES: biodiesel molar ratio of 0.5:1. When the DES: biodiesel molar ratio was increased to 1:1, the highest DGs removal was attained by DES 3 (100 %), followed by DES 4 (98.74 %) and DES 7 (98.17 %). The experimental DESs showed an average DG removal efficiency of 95.28 % which is comparably 49.5 % higher than that obtained by MTPB: glycerol DES [8].

From Table 3, it is clearly indicated that most of the DESs were not successful in removing TGs except for DES 7 which completely eliminated TGs at all ratios of DES: biodiesel. DES 6 also showed 100 % TGs removal at all DES: biodiesel ratio except for 1: 1. This phenomenon can be best explained by the mass transfer of other components between phases. Another possible explanation is trace amount of DESs that desorb in the temperature range of TGs [8]. In general, all tested DESs have higher tendency to reduce DGs than MGs and TGs. This phenomenon was consistent with the results obtained for MTPB-based DESs [8].

Table 3. Weight percentage of MGs, DGs, and TGs after extraction by all DESs.

DES: Biodiesel molar ratio	DES 1			DES 2			DES 3		
	MGs	DGs	TGs	MGs	DGs	TGs	MGs	DGs	TGs
0.5: 1	0.16	0.06	0.84	0.00	0.50	9.79	0.00	0.00	0.00
1:1	0.00	0.42	0.00	0.05	0.03	0.13	0.22	0.00	0.00
2:1	0.48	0.82	8.92	0.20	0.10	0.00	0.00	0.13	0.78
2.5:1	0.29	1.98	6.02	0.17	0.03	1.60	0.03	0.07	0.05

DES: Biodiesel molar ratio	DES 4			DES 6			DES 7		
	MGs	DGs	TGs	MGs	DGs	TGs	MGs	DGs	TGs
0.5: 1	0.07	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00
1:1	4.19	0.05	2.61	0.00	0.12	3.98	0.27	0.07	0.00
2:1	0.41	0.03	0.55	6.91	0.00	0.00	0.00	0.02	0.00
2.5:1	0.06	0.11	1.61	0.00	0.00	0.00	0.00	0.02	0.00

Based on the research work by Shahbaz, et al. [25], the binary DESs (ChCl: EG) had no considerable influence on the removal of MGs, DGs and TGs. These

findings prove the superiority of the new ternary DESs (ChCl: glycerol: ethylene glycol) for extracting the glycerides compared to conventional methods. In short, DES 7 is the best solvent to reduce glycerides as it reduced all glycerides below the EN standard.

3.5. Removal of total glycerol

According to Eq. (1), the total glycerol content in biodiesel depends on the amount of free glycerol, MGs, DGs, and TGs. The content of total glycerides before extraction was 0.9279 wt% which is higher than the limit specified by the EN 14214 and ASTM D6751 standards (0.25 mol% and 0.24 wt%, respectively).

As depicted in Fig. 4 and Fig. 5, all DESs reduced the total glycerol content below the ASTM standard with increasing DES to biodiesel molar ratio of 0.5:1 except for DES 2. When the DES: biodiesel molar ratio increased further, only DES 3 and DES 7 reduced the total glycerol below the standard. The maximum total glycerol removal of 100% is attained by DES 3 at 0.5 molar unit of DES: 1 molar unit of biodiesel followed by 99.75 % and 99.6 3% at DES 7: biodiesel molar ratio of 2:1 and 2.5:1 respectively. As observed from Fig. 5 and Fig. 6, when high amounts of DES were used to extract biodiesel, both DES 3 and DES 7 were able to remove more total glycerol. However, the optimum ratio of DES 3: biodiesel at 0.5:1 is chosen as it removed all free glycerol and glycerides at the minimum utilization cost.

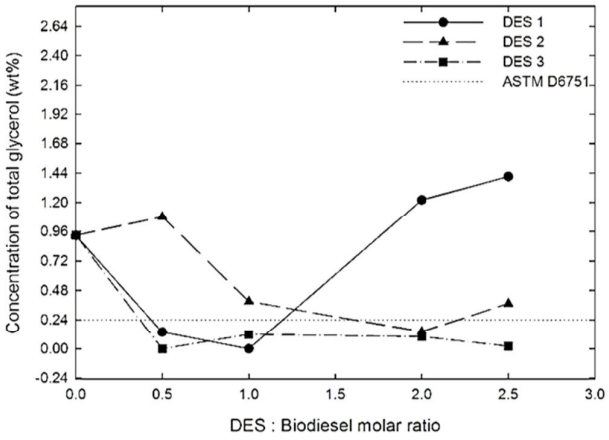

Fig. 4. Total glycerol removed by DESs (DES 1, DES 2 and DES 3).

In a previous study, Hayyan, et al. [5] reported that the ChCl: glycerol DESs could yield a maximum total glycerol removal efficiency of 16.2 %. On the contrary, ChCl: ethylene glycol DESs were more efficient in attracting total glycerol with maximum total glycerol efficiency of 30 % [25]. Later, it was reported the maximum total glycerol removal efficiencies for MTPB: glycerol DES and MTPB: ethylene glycol DES of 28 %, at the molar ratio of 2:1 (DES 1: biodiesel) and 40 % at the molar ratio of 3:1 (DES 4: biodiesel), respectively [8].

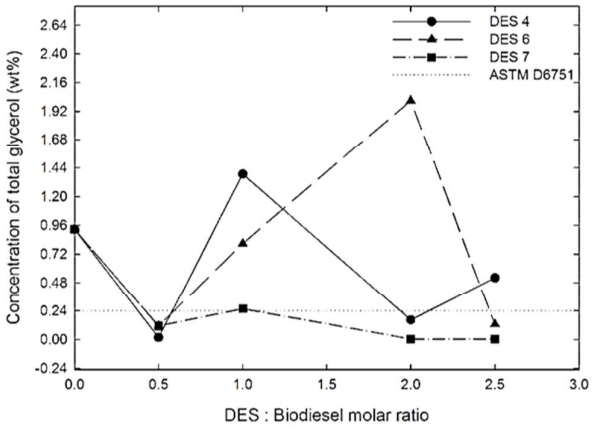

Fig. 5. Total glycerol removed by DESs (DES 4, DES 6 and DES 7).

In this work, the average total glycerol removal efficiency for the studied DESs was 81.43 % which is higher than both ammonium and phosphunium based DESs reported in the past studies. These findings have proven that the newly synthesized ternary DESs can yield higher glycerol removal efficiency at a minimum DES 3: biodiesel molar ratio of 0.5:1 as compared to other studied binary DESs. The high glycerol removal efficiency is due to the polarity of the newly synthesized DESs as strong hydrogen bonding formed between the hydrogen bond donors around the chloride anion of ammonium salt. Besides, the presence of hydroxyl group in both DES (solvent) and glycerol (solute) and the solvation force for glycerol in biodiesel resulted in a high affinity for the DES to attract glycerol through the hydrogen bonding and dipole-dipole interaction mechanisms [25].

4. Conclusion

In this work, seven new ternary DESs based on ChCl as salt while glycerol and ethylene glycol as hydrogen bond donors were selected as extraction solvents to eliminate glycerol from palm oil-based biodiesel. All DESs successfully formed as colourless liquids except for DES 5 which appeared as a turbid white liquid at ambient temperature and thus was not investigated further. The average water content of the studied DESs was found to be 0.1 wt%, which satisfied the maximum allowable limit (1 wt%). Furthermore, the studied DESs have freezing points lower than their constituting components complying to the universal characteristics of DESs. To further investigate the potential of the synthesised DESs as extraction solvents, the DESs were added to the produced biodiesel at different molar ratios of DES: biodiesel at ambient temperature. High average MGs, DGs and TGs removal efficiencies were observed (82.44%, 95.28% and 96.07%, respectively) and these outcomes justify the high performance of the new DESs as potential extraction solvents to remove total glycerol from palm oil-based biodiesel.

In addition, DES 3 and DES 7 showed excellent removal of free glycerol and total glycerol at all tested DES: biodiesel molar ratios except for the ration of 1:1.

The free glycerol and total glycerol were reduced below the required EN 14214 and ASTM D6751 international biodiesel standards using both DESs. The DES to biodiesel molar ratio (2:1 for DES 7), (2.5:1 for DES 7) and (0.5:1 for DES 3) were found to be the most effective ratios for reducing the total glycerol content with removal efficiencies of 99.63%, 99.75% and 100%, respectively. The optimum solvent to biodiesel molar ratio for all DESs was attained by DES 3. At a molar ratio of 0.5:1, DES 3 eliminated all free glycerol and glycerides with the minimum DES consumption.

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