

REMOVAL OF RESIDUAL CATALYST FROM PALM OIL-BASED BIODIESEL USING NEW IONIC LIQUIDS ANALOGOUS

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Abstract

Biodiesel is produced through transesterification of triglyceride and methanol in the presence of alkali catalyst to form glycerol and biodiesel. Purification methods are implemented to remove undesired products that are retained inside biodiesel. The purified biodiesel grade should adhere to international standard specifications EN 41214 and ASTM D6751. Residual potassium hydroxide (KOH) catalyst is one of the impurities in produced biodiesel which can be removed by deep eutectic solvents (DESs). DESs were formed by a salt and two hydrogen bond donors (HBDs). In this work, choline chloride (ChCl) was used as the salt while glycerol and ethylene glycol were used as the hydrogen bond donors. Six DESs were synthesized with various compositions of salt and HBDs to remove KOH catalyst. All DESs (DES1, DES2, DES3, DES4, DES6 and DES7) were successful to reduce KOH content in biodiesel. The results had demonstrated the removal efficiency of KOH increase with the increase of DES:biodiesel molar ratios and mole fraction of HBD in the mixture of DES. The optimum DES to biodiesel molar ratio for each DES was determined. The result had indicated DES4 as the best solvent for removal of KOH from biodiesel.

Keywords: Removal, Catalyst, Biodiesel, Transesterification, Deep eutectic solvent.

Nomenclatures**Abbreviations**

ChCl	Choline chloride
DES	Deep eutectic solvents
DSC	Differential scanning calorimeter
EG	Ethylene glycol
FAME	Fatty acids methyl esters
FFA	Free fatty acid
GL	Glycerol
HBD	Hydrogen bond donor
ICP-OES	Inductively coupled plasma-optical emission
ILs	Ionic liquids
KOH	Potassium hydroxide
NaOH	Sodium hydroxide
RBD	Refined, bleached, deodorised

1. Introduction

The industrial sector and transportation sector have been classified as the first and second largest energy consumption sector in global. It has been accounted that the transportation sector could cover up 60% of the oil in the world thus resulting in substantial growth of oil demand. There are approximately 97.6% of oil is used as the fossil fuel for transportation sector with traces amount of natural gas [1].

Biodiesel as a renewable energy has been receiving much attention to overcome these problems due to its environmental benefits and its sources which derived from animal fats, plant oils, wastes or renewable sources such as cooked vegetable oils. It has several advantages over biodiesel to fossil fuel as being biodegradable, renewable, emit slight amount of carbon dioxide (CO₂) with no net addition to atmospheric CO₂ level thus decreases global warming issues. Besides, biodiesel has high combustion efficiency due to its properties likely the same with fossil based biodiesel which has high cetane number and flash point. Biodiesel has low sulfur and aromatic content yet it possesses high energy content [2-4].

Four major methods are used to produce biodiesel, for example direct-use or blending of oils [5, 6], microemulsion [7], thermal cracking [8, 9] and transesterification [10]. Figure 1 shows the most common method in biodiesel production, which is transesterification of triglyceride and alcohol in the presence of alkali catalyst to form glycerol and fatty acids alkyl esters (FAAE). Triglycerides are the main components in vegetable oils. Methanol is the common alcohol utilized by the industries due to low cost and good chemical properties which helps in producing low viscosity of biodiesel [11]. Potassium hydroxide (KOH) is used as the alkali catalyst due to its high conversion rate in transesterification reaction [12]. The viscosity of triglycerides is generally reduced after transesterification reaction; as a result improve the physical properties of biodiesel [13].

Transesterification reaction can be categorized into acids, alkalis and enzymes catalytic transesterification. Enzyme-catalyzed transesterification has its own advantages. It is able to produce high yield of methyl esters, absence of side reactions and ease up glycerol recovery to produce high grade of glycerol [14,

15]. Moreover, enzyme-catalyzed transesterification is applicable for feedstock with free fatty acid (FFA) ranging from 0.5% to 80% [16, 17]. Nevertheless, enzyme-catalyzed transesterification is not commercialized due to high lipase catalyst's production cost, longer reaction time as compare to alkali-catalyzed transesterification reaction as well as limitation of regeneration and reuse of biocatalysts within a long operating time [10, 14]. Acid and alkali catalyzed transesterification are utilized in biodiesel production typically. The acid-catalyzed transesterification reaction is sensitive to the presence of water. Canakci and Gerpen et al. [18] revealed that concentration of water at 1 g kg⁻¹ presence in the reaction mixture can affect the yields of ester in the transesterification of vegetable oil. When the water concentration reaches to the point of 50 g kg⁻¹, transesterification reaction is completely inhibited. More disadvantages of homogeneous acid catalytic transesterification include equipment corrosion, produced wastes from neutralization process, difficult to recycle, formation of secondary products, higher reaction temperature, long reaction times, slow reaction rate, weak catalytic activity and elaborate engineering process [19].

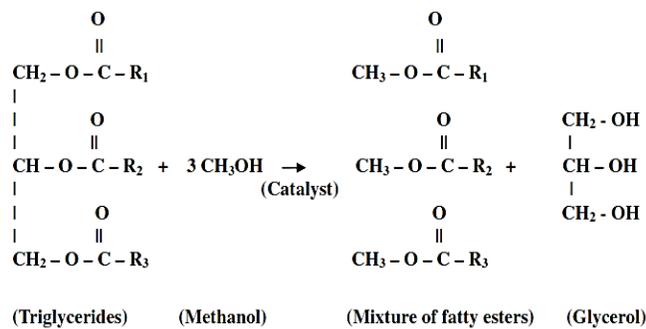


Fig. 1. Transesterification reaction.

The best biodiesel production is achieved by using homogeneous alkali catalyst [20]. Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are common catalysts used in the alkali-catalyzed transesterification [21]. This method produces high yield of fatty acid methyl esters (FAME) from triglycerides at high conversion rate within a short reaction time (30-60 min) [1, 14]. Alkali-catalyzed transesterification can be carried out at ambient pressure and moderate temperature range of 40-60°C with low catalyst concentration range of 0.5-2.0 wt%. Alkaline catalytic method is the most efficient and economical catalytic method than other method. The conversion rate of an alkaline catalyst is approximately 4000 times faster by comparing it with same amount of acid catalysts use in transesterification reaction [22, 23].

On the other hand, alkali-catalyzed reaction has its disadvantages as well. These drawbacks include the high consumption of energy, difficult to have recovery of glycerol, requirement of treating alkaline wastewater after reaction, interference of FFA and water during the reaction as well as occurrence of undesirable side reaction due to low selectivity [14-15, 24]. Homogeneous base

catalytic transesterification requires post reaction separation of catalyst, by-product and product at the end of the reaction which increases biodiesel cost. During transesterification process, saponification will occur if significant amount of FFAs found in the vegetable oils react with the alkali catalyst. As a result, separation of final product into biodiesel and glycerol becomes more difficult. Subsequently, wastewaters produce from purification of biodiesel (water washing) increase [21]. The presence of water content in vegetable oils also contributes to the happening of saponification. Soap produced consumes some of the alkali catalyst thus reduced the efficiency of catalyst in the transesterification reaction. The formation of gels from the soap decreases the yield of methyl ester (biodiesel) and makes the separation of glycerol more difficult [25].

Impurities contain in produced biodiesel include free glycerol, residual KOH catalyst, methanol, water and soap. These impurities can decrease the performance of the car engine. Thus, several stages of purification method for example evaporation of residual methanol, neutralization reaction and water washing are require to remove the impurities in biodiesel before commercializing the biodiesel to market.

The presence of residual KOH catalyst in produced biodiesel can cause carbon residue deposited in fuel injection system. Consequently, these carbon residues could poison the emission control system. Besides, residual KOH catalyst induces engine filter blockages therefore reduce the engine performance in general [26]. In addition, the presence of residual KOH catalyst reduces the quality of biodiesel.

Therefore, biodiesel purification process is an essential. Biodiesel purification methods can be categorized into three major methods, i.e. water washing, dry washing and membrane extraction [26, 27]. In general, water washing method uses water as the medium to dissolve impurities in biodiesel. Washing step is repeated a few times until clear water phase is observed. Water washing has several disadvantages which are high production cost, high energy consumption, long production time, production of polluting liquid effluent, also considerable loss of desired product due to retention in water phase [28]. On the other hand, dry washing method used ion exchange resin or magnesium silicate powder as an adsorbent to remove impurities. Unfortunately, the purified biodiesel grade after dry washing cannot accomplish specification limit set by the international standard EN 14214. Dry washing method increases the production cost due to the expenses of added material in purification process. Another purification method is membrane extraction. Membrane extraction performs a liquid-liquid extraction to remove impurities. However, cost of material used in membrane extraction is expensive, also high flow rate of material stream causes fouling effect in the membrane.

Deep eutectic solvent (DES) is characterized as a mixture of two or more inexpensive and benign components that associated by hydrogen bond interactions to form eutectic mixtures [29]. They exit as liquid phase below 100°C due to the large freezing point depression resulted from strong hydrogen bond [30] In general, DES can be synthesised from organic halide salts and hydrogen bond donors [2].

Shahbaz et al. explored another application of DES in removing residual catalyst KOH from palm oil-based biodiesel. His team demonstrated DESs that are made from CHCl_3 and glycerol are successfully in removing residual KOH and water content lower than the limit set by the EN 14214 and ASTM D6571 [31].

Besides, the researcher also discovered that new combination of DESs from ammonium salt: ethylene glycol at 1:2.03 molar ratio has higher efficiency in eliminating total glycerol compared to conventional ammonium salt: glycerol. It is projected that the new ternary DESs composed of ChCl, glycerol and ethylene glycol have the capabilities to remove both glycerol and residual KOH in produced biodiesel. Also, some ternary DES exhibits lower freezing point than binary DES of the similar components which is more advantageous in industrial application [32]. In this project, the new DESs (ChCl: glycerol: ethylene glycol) are investigated as solvent to remove KOH catalyst to below the permissible level set by EN 14214 and ASTM D6751 biodiesel international requirement.

2. Experimental Section

2.1. Materials

Palm oil is widely available in Malaysia, also, it is found abundant in South East Asian countries [33]. Palm oil-based biodiesel possess highest cetane number among other vegetable oils could provide better ignition quality for diesel engine [14, 34-35]. For these reasons, palm oil is chose as the raw material in transesterification reaction to produce biodiesel. RBD palm oil is utilized in this work due to trace amount of impurities that contain inside the RBD palm oil. RBD palm oil (Yee Lee Sdn Bhd) was obtained at the local mart.

Chemicals such as methanol and potassium hydroxide pellets with purity of 99.8% and 98.9% respectively were purchased from Merck, Malaysia mainly for biodiesel production. For synthesis of DES, choline chloride salt ($C_5H_{14}ClNO$) and glycerol ($C_3H_8O_3$) and ethylene glycol ($C_2H_6O_2$) as two hydrogen bond donors (HBDs) with high purity (>99%) were purchased from Merck, Malaysia. These three chemicals are used to synthesize DESs without further purification. Mass fraction of water in these chemicals is < 10⁻⁴ as per the guide from the manufacturer.

2.2. Production of palm oil-based biodiesel

500 g of RBD palm oil was added into a beaker and was heated up by using water bath (Daniel DNP 9051) to carry out alkali catalyzed transesterification reaction. Potassium hydroxide as a catalyst (1wt% of palm oil) was mixed with methanol to form potassium methoxide. The homogeneous potassium methoxide solution was added into the beaker which operating at a reaction temperature of 333.15 K. Molar ratio of palm oil to methanol was 1:10 (methanol in excess) was prepared in this experiment to increase yield of product. The mixture was stirred by an agitator at a constant speed of 400 rpm. After the mixing for 2 hours, the mixture was cooled to room temperature and was then poured into a separation funnel. Two layers of liquids will be formed after overnight settling. The biodiesel phase at the upper layer was separated from the rich glycerol phase at bottom layer.

2.3. Deep eutectic solvents (DESs) synthesis

In this work, choline chloride (ChCl) was used as the salt while glycerol and ethylene glycol were selected as the HBD to synthesize seven ternary DESs with

various compositions. 20 g of ChCl was prepared and the mass of HBDs were varied based on the specified molar ratios in each synthesized DES. The mass of each chemical was measured precisely by using weighing balance Shimadzu TX423L. DES mixture was added into screw cap vial and a magnetic stirrer was put into the vial to homogenize the mixture. The screw cap vial was sealed with parafilm to prevent moisture from surrounding air contacting with DES in the vial. DES mixture was heated up to 80°C on a hot plate stirrer (IKA C-MAG HS 7) and was stirred at 300 rpm for one hour until a homogeneous colourless liquid phase was obtained. Table 1 shows the molar ratios of salt and HBDs in different DES.

Table 1. Molar ratios of salt and HBDs in each synthesized DES.

Abbreviation	Molar ratio		
	ChCl	Glycerol	Ethylene glycol
DES1	1	1	1
DES2	1	2	1
DES3	1	1	2
DES4	1	2	2
DES5	2	1	1
DES6	2	2	1
DES7	2	1	2

2.4. Characterization of deep eutectic solvents

2.4.1. Freezing temperature

Mettler Toledo Differential Scanning Calorimeter (DSC 1 STARe System) is used to measure the freezing points of all the samples of DES. The instrument is first calibrated against known standards using water and 2-propanol to assure the accuracy of measurement before carrying out the experiment.

2.4.2. Water content

Karl Fisher titration method is employed to determine the water content of all the DESs. The instrument is calibrated against the known standard using Hydranal-water standard 1.00 mg/g to ensure the measurement accuracy of the Karl Fisher coulometer.

2.5. Extraction of residual KOH catalyst using DESs

Liquid-liquid extraction process is performed in removal of KOH catalyst in biodiesel phase. Each synthesized DES was added to the biodiesel phase which separated from glycerol-rich phase at different molar ratios (ranging 0.5, 1.0, 2.0, 2.5 mole DES per 1 mole biodiesel). The samples were agitated at 200 rpm using an orbital shaker for 1 hour at ambient temperature. After 2 hours of settling, the upper layer of purified biodiesel is removed from the used DES for KOH content analysis using inductively coupled plasma-optical emission (ICP-OES).

2.6. KOH content analysis

The residual KOH catalyst in final product (after extraction process) was measured using the PerkinElmer Optima 7000 DV ICP-OES instrument (PerkinElmer, Inc., Shelton, CT, USA). ICP-OES instrument is equipped with WinLab 32 utilizing argon (99.99%) as the carrier gas to measure the content of potassium in biodiesel. Table 2 shows the ICP-OES analytical condition while doing the sample analysis. The wavelength is set at 766.486 nm for the analysis of potassium content. The oil standard for potassium (500 mg/kg) was diluted in xylene solution (Merck, >99%) at five various concentrations (0.1, 0.25, 0.5, 0.75 and 1 ppm). The oil based in this work was supplied by Conostan Company. The solutions of different concentrations were inserted into the ICP-OES to conduct the calibration. Linear correlation coefficient (R_2) was obtained and the result show a good linearity of 0.998. All purified biodiesel samples were injected into ICP-OES to determine the potassium content after the determination of potassium peak area. The potassium content in all biodiesel samples was calculated with reference to calibration.

Table 2. ICP analytical conditions.

Plasma gas flow	15 L/min
Auxiliary gas flow	1.5 L/min
Nebulizer gas flow	0.45 L/min
RF power	1450 W
Pump flow rate	1 mL/min
Read delay	90 s
Processing	Peak area
Replicates	3
Torch	Quartz for axial view

3. Results and Discussions

3.1. Biodiesel synthesis

The palm oil-based biodiesel was synthesized through alkali catalyzed transesterification of triglycerides with methanol in the presence of alkali catalyst which is potassium hydroxide (KOH). The produced biodiesel was not purified in the washing column; it was analysed by ICP-OES directly. Table 3 shows the results of ICP-OES for the analysis of KOH content in produced biodiesel before extraction using the DESs. 69.978 mg/kg of KOH content was detected in unpurified biodiesel which has over the limitation set by the international standards EN 14214 and ASTM D6751 (5 mg/kg).

Table 3. KOH content of unpurified biodiesel.

Attributes	KOH content (mg/kg)
Produced biodiesel	69.98
EN 14214	5
ASTM D6751	5

3.2. DES synthesis

Choline chloride (ChCl) was mixed with two different hydrogen bond donors: glycerol and ethylene glycol at seven different molar ratios to form seven ChCl

based DESs (DES1 – DES7). The chemicals combination ChCl: glycerol DES was chosen due to its high removal efficiency of KOH catalyst; on the other hand, ChCl: ethylene glycol DES can eliminate high amount of glycerol from palm oil-based biodiesel [31, 36]. DES molar ratios were used based on lowest freezing point attained for the combination of salt to HBD. During the synthesis of DES, salt:HBD mixture had formed a white viscous gel during the first 20 minutes of mixing process. A clear liquid phase with some undissolved salt was then formed after another 30 minutes of mixing. A continuous of mixing process was required until a homogeneous liquid phase of DES was observed. Colourless liquid was appeared in all the newly synthesized ternary DESs at the ambient temperature except for DES5. DES5 appeared as a cloudy white liquid phase or a colourless mixture of solid and liquid based on the temperature of the mixture. The existence of solid sediment at the bottom of the mixture revealed that the quantity of salt was in excess corresponding to the HBDs (2:1:1 ChCl:glycerol:ethylene glycol). This condition also expressed that DES5 does not reach to the eutectic point at that given salt:HBD:HBD molar ratio. Stronger hydrogen bonding was achieved between salt and hydrogen bond donors by increased the amount molar ratio of hydrogen bond donors as described in DES2, DES3, DES4, DES6, and DES7. All DESs had complete dissolution except DES5 thus DES5 was not studied further and was not taken as extraction solvent in this work.

Table 4 shows the freezing point for all synthesized DESs. It has been reported that all synthesized DESs have lower freezing points than their constituting components. The freezing temperatures of synthesized DESs are basically below the room temperature. This property has in turn indicated the normal behaviour of DES. In addition, it can be observed that hydrogen bond donors had shown its large contribution in lowering freezing point of DES by strengthens salt: HBD hydrogen bonding interactions and by decrease its lattice energy. This can be observed where freezing temperature of DES significantly decreases as the hydrogen bond donors' molar ratio increase. Besides, water content of all synthesized ChCl based DESs was studied. As shown in Table 4, the water content of all newly synthesized DESs are slightly higher than 0.1 wt% except for DES 1 and DES 6 which has water content of 0.0908 wt% and 0.0959 wt% respectively. The average water content of all synthesized DESs was 0.1 wt% which was consistent with the physical properties of deep eutectic solvents (1 wt%).

Table 4. Freezing Point and Water Content of All DESs.

DES	Freezing temperature (°C)	Water content (mg/kg)
1	8.36	908
2	-4.28	1018
3	-18.06	1158
4	-23.75	1303
6	12.25	959
7	22.77	1189

3.3. Removal of KOH residues from biodiesel

Synthesized DESs were added into produced biodiesel at four different molar ratios of DES to biodiesel (0.5:1, 1:1, 2:1 and 2.5:1) to determine maximum

removal efficiency of residual catalyst in biodiesel. DES: biodiesel were mixed for one hour. The extraction process was then carried out at room temperature. After two hours of settling, two layers are formed due to the density difference where the upper phase was purified biodiesel and bottom phase was spent DES. It was detected that the DES layer is immiscible with biodiesel phase so it can be wholly separated from the biodiesel. The purified biodiesel phase was analysed by using ICP-OES for its KOH content through measuring the concentration of potassium element in the biodiesel. Calibration for ICP-OES was done before injecting the sample for analysing. The result had indicated a perfect linearity as the linear correlation coefficients (R_2) has shown a value which was greater than 0.99.

Figures 2 and 3 demonstrate the results for KOH content in biodiesel after extraction using all studied DESs. The KOH content in biodiesel before extraction was 69.98 mg/kg which was incredibly higher than maximum concentration as specified by EN 14214 and ASTM D6751 (5 mg/kg). All studied DESs were able to reduce KOH content below the standard at 1:1 DES: biodiesel molar ratio except for DES1, DES3 and DES7.

In general, the increase of DES: biodiesel molar ratio up to 2.5 shows excellent KOH extraction for all DESs except for DES1. All DES: biodiesel molar ratios for DES1 could not meet the EN 14214 and ASTM D6751 standard. Figure 2 has shown all DES:biodiesel molar ratios for DES1 were failed to remove KOH content in biodiesel. Same condition goes to low DES:biodiesel molar ratios (0.5:1 and 1:1) for DES3. On the other hand, all DES:biodiesel molar ratios of DES2 were successfully reduce the KOH content in biodiesel below EN 14214 and ASTM D6751 standard test limit. It was also detected that higher molar ratios of DES:biodiesel in DES3 (2:1 and 2.5:1) had successfully reduced KOH content from biodiesel. The removal efficiency of KOH using DES1, DES2 and DES3 were above 93.33%. It can be observed in Fig. 2, the optimum KOH removal was attained by DES2 which removed all KOH content at lowest DES: biodiesel molar ratio of 0.5:1.

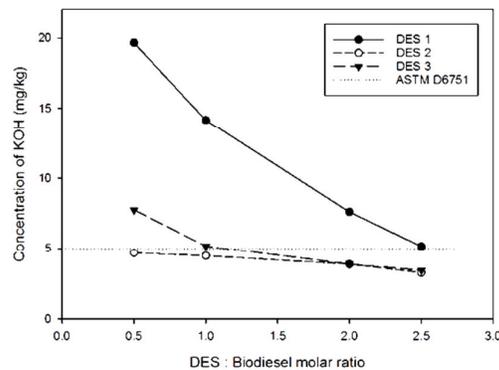


Fig. 2. Removal of KOH after extraction by [ChCl:glycerol:ethylene glycol] DES1, DES2 and DES3.

ICP results for KOH removal by DES4, DES6 and DES7 were shown in Fig. 3. All DES4:biodiesel molar ratios (0.5:1, 1:1, 2:1 and 2.5:1) were perfectly reduced KOH content in biodiesel below the standard limitation. Low DES: biodiesel molar

ratio (0.5) in DES6 did not provide a good KOH removal efficiency. However, it is noticeable that removal efficiency of KOH was improved with the increase of DES: biodiesel molar ratio. Hence, higher DES: biodiesel molar ratios from DES6 (1:1, 2:1 and 2.5:1) and two higher DES: biodiesel molar ratios from DES7 (2:1 and 2.5:1) could reduce KOH content below EN 14214 and ASTM D6751 specifications. The maximum removal efficiency of KOH content in biodiesel was found at 2.5:1 DES: biodiesel molar ratio in all studied DES. DES2, DES3, DES4, DES6 and DES7 have a maximum removal efficiency of 95.34%, 95.09%, 98.61%, 96.00% and 97.48%, respectively.

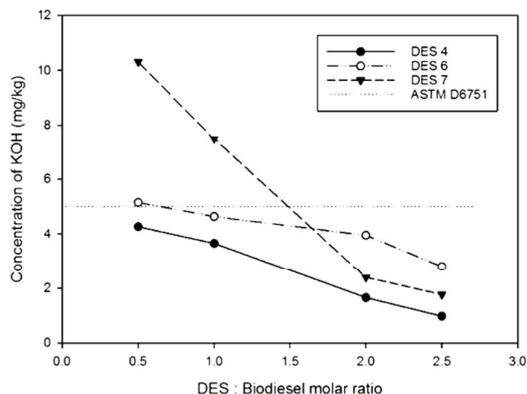


Fig. 3. Removal of KOH after extraction by [ChCl:glycerol:ethylene glycol] DES4, DES6 and DES7.

Apart from the increase of KOH removal efficiency by the increase of DES to biodiesel molar ratio, one of the elements which can affect the extraction performance is the composition molar ratio of DES. When the molar ratio of glycerol in DES increases from 1 to 2 (DES1 and DES2 in Fig. 2), the removal efficiency of KOH increases. This outcome is reinforced by the research work completed by Shahbaz et al. [31] in which glycerol-based DESs have larger impact in removal of residual catalyst. Besides that, the increase of molar ratio of ethylene glycol had also resulted in an incremental improvement of KOH removal in biodiesel. KOH removal efficiency increases when the molar ratio of ethylene glycol in DES increases from 1 to 2 (DES 2 and DES 4 in Fig. 4). In this research work, the average removal efficiency of KOH using ternary DES is 92.14 %.

As shown in Fig. 4, all DES: biodiesel molar ratio of DES2 and DES4 were successfully reduced KOH content in biodiesel to the permissible level. DES2 has molar composition ratio of 1 mole of salt, with 2 moles of glycerol and 1 mole of ethylene glycol while DES4 has molar composition ratio of 1 mole of salt, with 2 moles of glycerol and 2 mole of ethylene glycol. It is not difficult to discover that both DESs have similar glycerol molar composition ratio. Because KOH has high solubility in glycerol, it resulted in increase of DES capability to dissolve more KOH in DES. Hence DES2 and DES4 can easily remove large amount of residual catalyst from biodiesel at very low DES: biodiesel molar ratio.

0.5: 1 up to 2.5:1 DES: biodiesel molar ratios were used in this project. In fact, the use of higher DES: biodiesel molar ratios (e.g. 3.0 to 10.0) can be used in

order to increase the removal efficiency of KOH catalyst in biodiesel. However, by observing the exponential trends in Figs. 2 and 3, the increment of removal efficiency of KOH using higher DES: biodiesel molar ratio may be little or no increment at all. In addition, DES will be present in excess corresponding to biodiesel when more DES molar ratios are added. According to Figs. 2 and 3, all studied DESs were successfully to reduce KOH content below the international standard specification using DES: biodiesel molar ratios of 2.0. Hence, it is not necessary to increase DES: biodiesel molar ratio since this molar ratio had given good removal efficiency. In addition, it is not cost effective to increase DES: biodiesel molar ratios to higher values with little increment of KOH removal efficiency as higher DES: biodiesel molar ratio will require higher amount of ChCl, glycerol and ethylene glycol when synthesizing DES. As a result, capital cost of project increases.

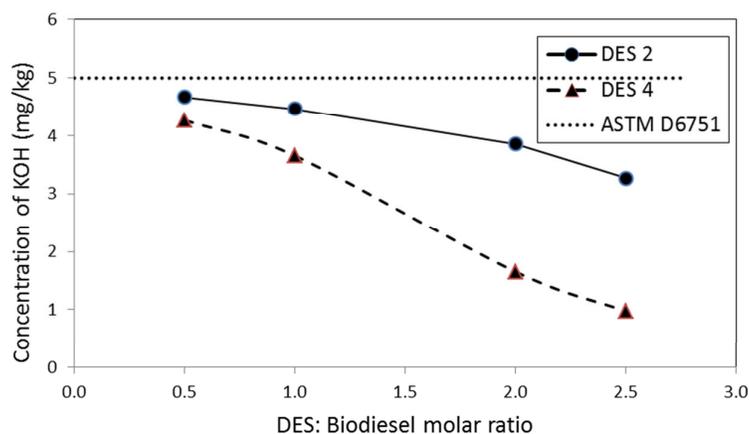


Fig. 4. Comparison of removal efficiency of DES2 and DES4.

Intermolecular attraction took place between solvent (DES) and solute (KOH). Intermolecular attractions include hydrogen bonding, ion pairing, dipole and Van der Waals interactions. High removal efficiency of KOH using DES is basically due to the polarity of ternary DES to form hydrogen bonding between hydrogen bond donors with chloride anion in ammonium salt. Because of the polarity of DESs and the presence of hydroxyl group in both DES and KOH as well as the solvation force of KOH in biodiesel, DESs have high affinity to the attraction of KOH as dipole-dipole attraction and hydrogen bonding was taken place during extraction process [36].

According to the research work done by Atadashi et al. [37], the author had revealed that the KOH content in biodiesel had been reduced by 96.25% after the separation process using ultra-filtration membrane technology. The initial content of KOH in palm oil-based biodiesel before membrane separation was 9.607 mg/kg. After the separation process, the KOH content was then reduced to 0.36 mg/kg. However, there was formation of saturated membrane after a few cycles run of biodiesel through ultra-filtration membrane. Removal efficiency of KOH was decreased along with repeated membrane separation process. This result had

in turn contributed to the use of DES as extraction solvent where spent DESs did not decreasing much efficiency to extract KOH catalyst for few cycles of extraction process continuously [31].

DES2, DES3, DES4, DES6 and DES7 were able to reduce KOH content to below the ASTM and EN standard at the minimum DES usage. Table 5 shows the optimum molar ratios for all used DESs with the corresponding removal efficiency of KOH. DESs which have similar optimum DES: biodiesel molar ratio was compared in terms of KOH removal efficiency. The comparison result had finalized DES4, DES6 and DES7 as the three best DESs to remove residual catalyst from biodiesel. The optimum DES in this project was rule by the DES performance which gave high KOH removal efficiency with the minimum usage of DES. Hence, it can be concluded that the optimum molar ratio of all studied DESs in removal of KOH catalyst was undertaken by DES4 at 0.5:1 DES to biodiesel molar ratio as it removed residual catalyst below the standard specification at the minimum usage of DES.

Table 5. Optimum molar ratios of DESs to remove KOH.

DES	Optimum molar ratio (DES:biodiesel)	Removal efficiency (%)
1	-	-
2	0.5:1	93.3%
3	2.0:1	94.5%
4	0.5:1	93.9%
6	1.0:1	93.4%
7	2.0:1	96.6%

4. Conclusion

In this work, we had presented and examined a new purification method for the removal of residual KOH catalyst from palm oil-based biodiesel by using ammonium-based DESs. Seven ChCl-based DESs with different compositions of HBD were synthesized and were examined as new solvents to remove KOH catalyst.

Synthesized DESs were added into palm oil-based biodiesel at different molar ratio of DES: biodiesel at room temperature. Shahbaz et al. [31] who employed binary DES to eliminate residual catalyst reported that ChCl: glycerol and ChCl: ethylene glycol DESs have certain impact on the removal of residual KOH catalyst. All studied DESs in this work have an average removal efficiency of 92.14 % where the highest removal efficiency was achieved at the highest DES: biodiesel molar ratio (2.5) in each synthesized ternary DES. The experimental KOH removal efficiency obtained was also higher than ultra-filtration membrane separative technology contributed by Atadashi et al. [37]. This outcome has supported the advantages of new ternary DESs as potential extraction solvent to eliminate residual catalyst from palm oil-based biodiesel.

In addition, all tested DES: biodiesel molar ratio of DES2 and DES4 demonstrated excellent removal of KOH in biodiesel. Both DESs were successfully reduced the amount of catalyst to permissible level set by EN 14214 and ASTM D6751 international biodiesel standards. DES: biodiesel molar ratio (2.5: 1 for DES6), (2.5: 1 for DES7) and (2.5: 1 for DES4) were disclosed as the most effective extraction solvent which has removal efficiency of 96.00%, 97.48% and 98.61% respectively. The optimum molar ratio of all studied DESs in

removal of KOH catalyst was undertaken by DES4 at 0.5:1 DES to biodiesel molar ratio as it removed residual catalyst below the standard specification at the minimum usage of DES.

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