Purification of Palm Biodiesel Using Deep Eutectic Solvent (DES) Based Choline Chloride (ChCl) and 1,2-Propanediol (C₃H₈O₂)

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Abstract. The development of environmentally friendly technologies is now gaining important attention in the field of chemistry, one of which is the development of environmentally friendly organic solvents. Deep eutectic solvent (DES) is potential as an environmentally-friendly solvent because it is non-toxic, non-reactive with water, biodegradable, low melting point and easy and inexpensive synthesis to produce high purity DES. This study was aimed to test the potency and effectiveness of Deep Eutectic Solvent (DES) based choline chloride: 1,2-propanediol as co-solvent in biodiesel purification. DES used on the basis of Choline Chloride (salt) and 1,2-Propanediol (HBD) with a 1:2 and 1:3 molar ratio were applied to purification of biodiesel at concentration of 1; 5; 10; and 15% (w/w). And then will be compared between methanolysis and ethanolysis process. From the result of the research, it found that DES based ChCl / 1,2 Propanediol has good freezing point, density, and viscosity as solvent and can increase ester content or purity and yield of biodiesel in purification process. The highest purity of biodiesel was 98,88% at ethanol to oil molar ratio of 9:1 and 5% DES in ethanolysis process.

1. Introduction
Nowadays, environmentally friendly technology receives important attention in the field of chemistry, it aims to preserve the environment and reduce the negative effects of its use. Eco-friendly technology helps reduce harmful media usage by controlling the physical properties of media, such as temperature and pressure [1].

With the advent of such environmentally friendly technologies, many researchers are interested in developing environmentally friendly organic solvents [2]. Over the past few decades, ionic liquid (IL) are one of the most environmentally friendly organic solvents that attract attention because of their unique physical properties, low melting point, low volatility, high thermal stability, high polarity, good stimulation, suitable for a variety of solubilities and have good ability for reuse [3,4].

However, there are problems in the widespread use of IL, which are high costs, low purification, toxicity and biodegradability problems [3,2]. This makes IL unavailable for industrial scale and the high cost of synthesis is a constraint of its widespread use in industry [5,6]. Recently, alternative solvents for IL has been found, namely deep eutectic solvent (DES) [5]. DES has advantages in terms of cost and environmental impact compared to IL and its synthesis has been widely developed [7]. DES is synthesized from a mixture of organic halide salts with an organic compound as a donor bond of hydrogen / hydrogen bond donor (HBD) capable of forming a hydrogen bond with a halide ion [8].
DES is being widely used in research and industry because of its potential as an environmentally friendly solvent, non-toxic, non-reactive with water, biodegradable, low melting point and easy and inexpensive synthesis to produce high purity DES [8,9]. DES has been applied in various fields including as a catalyst in the field of biology, organic synthesis, dissolution and extraction processes, chemicals and electrochemistry [9]. In addition, DES is currently widely applied in the field of biodiesel synthesis, such as a solvent in the removal of catalysts from biodiesel [6], as a solvent in the removal of glycerol from biodiesel [8], as a medium in biodiesel synthesis of enzymatic reactions [10] and as co-solvent in biodiesel synthesis [11].

Recent studies have shown the use of DES as a solvent and a catalyst in methanolysis can improve yield and facilitate purification [12]. Besides being used to reduce the use of solvents in the transesterification process, DES can be used in purification of crude biodiesel to increase the methyl ester content and yield of biodiesel produced. Hayyan, et al. (2010) reported that using ChCl-based DES can extract to 51% of glycerol from biodiesel with Refined Palm Oil (RPO) [13]. Hayyan, et al. (2014) also reported that use of DES-based ChCl can increase FAME conversion of 96% and yield of 97% with Acidic Crude Palm Oil (ACPO) [5]. Shahbaz, et al., (2011) also reported that use of ChCl-based DES can exclude KOH from the remaining reaction of transesterification to 98.59% with Crude Palm Oil (CPO) [6]. The utilization of ethanol also presents inconveniences. Effectively, it indicated in the literature, the base-catalyzed formation of the stable emulsion during ethanolysis is a problem [12].

The use of choline chloride based DES can be used to purify of biodiesel from impurities, such as residual catalyst, glycerol, and unreacted oil residue. However, no studies have examined the use of choline chloride and 1,2-propanediol based DES as a co-solvent in the purification of biodiesel through transesterification reaction. So, in this paper will be discussed the effect of addition of DES in purification of biodiesel.

2. Experimental Details

2.1. Synthetic of DES
This study used a DES-based ChCl as ammonium salt and 1,2-propanediol as Hydrogen Bond Donor (HBD). The synthesis of deep eutectic solvents (DES) was performed with a variable of 400 rpm stirring rate with a reaction temperature of 80 °C for 2 hours. The molar ratio of ChCl: 1,2-propanediol is 1:2 and 1:3.

2.2. Preparation of Biodiesel
The material used is crude palm oil and performed pretreatment with degumming process of palm oil using phosphoric acid become Degummed Palm Oil (DPO). The transesterification reaction for biodiesel process was performed with a fixed variable, stirring of 300 rpm at temperature of 65 °C for 1 hour with a molar ratio of methanol: DPO of 6: 1, ethanol: DPO of 9: 1 and a catalyst concentration of 1% for methanol and 1.2% for ethanol, and the variables of DES concentration (0, 1, 5, 10, and 15%). In the biodiesel purification process, DES with a certain concentration is mixed into crude biodiesel and stirred for 5 minutes at 400 rpm.

2.3. Product Analysis
The analysis of biodiesel includes of Density (Indonesian National Standard), Kinematic Viscosity (ASTM D 445), Acid Numbers (AOCS Cd 3d-63 or Indonesian National Standard of 7182-2015), Soap Numbers (AOCS Cd 3-25 or Indonesian National Standard of 7182-2015), Total Glycerol (AOCS Ca 14-56 or Indonesian National Standard of 7182-2015) and ester content using Gas Chromatography instrument (Type 122-5711, Durabond-5HT).
3. Result and Discussion

3.1. Characteristics of Deep Eutectic Solvent (DES)
From the results of DES synthesis with ChCl/1,2-propanediol at molar ratio of 1:2 and 1:3 produces a colorless liquid form at room temperature so it can be used as a solvent in the next process.

3.2. The Effect of DES to Acid Number of Biodiesel
Analysis of the effect of DES in the purification of biodiesel on the acid number of biodiesel is done by applying different concentration of DES with different ratios and comparing it with the acid number of biodiesel without DES. The acid number of methyl ester biodiesel without using DES is 0.00167 mg/g and 0.00165 mg/g of ethyl ester biodiesel. Acid number of biodiesel can be seen in Fig.1. and Fig. 2. below:

![Figure 1. The Effect of DES to Acid Number of Biodiesel at DES Molar Ratio of 1:2](image1)

![Figure 2. The Effect of DES to Acid Number of Biodiesel at DES Molar Ratio of 1:3](image2)

Based on the Figure 1 above can be seen that the resulting graph fluctuates for methyl ester and ethyl ester. Same as the Figure 2, acid number of methyl ester and ethyl ester biodiesel show a fluctuating graphic.

The acid number is the amount of KOH (mg) required to neutralize the free acid in the sample weight used. The acid number is an important parameter as one of the indices of biodiesel quality. This is because the acid number has the potential to corrosion the engine vehicle, this is due to the high oxidation process [13].
Increased acid number in some DES variations may be due to the pH of the DES itself (ChCl or 1,2-propanediol), such as ChCl having an acidic pH (pH 5). Then testing on some of the resulting DES, has an acidic pH as well, so it is likely to increase the acid number of biodiesel.

From Figure 1 and Figure 2 it can be seen that DES is more optimal in reducing of acid numbers with a certain concentration in biodiesel by using ethanol than methanol. And the more optimal in reducing the acid number is at the molar ratio of 1: 2, this is because at the ratio it can be seen that the acid number becomes lower than that which does not use DES although the result is not constant.

3.3. The Effect of DES to Total Glycerol of Biodiesel
Analysis of the effect of DES in the purification of biodiesel on the total glycerol of biodiesel is done by applying different concentration of DES with different ratios and comparing it with the total glycerol of biodiesel without DES. The total glycerol of methyl ester biodiesel without using DES is 0.238% and 0.289% of ethyl ester biodiesel. Total glycerol of biodiesel can be seen in Figure 3 and Figure 4 below:

![Figure 3](image3.png)

**Figure 3.** The Effect of DES to Total Glycerol of Biodiesel at DES Molar Ratio of 1:2

![Figure 4](image4.png)

**Figure 4.** The Effect of DES to Total Glycerol of Biodiesel at DES Molar Ratio of 1:3

In Figure 3 above can be seen that the resulting graph fluctuates for methyl ester and ethyl ester. Same as the Figure 4, total glycerol of methyl ester and ethyl ester biodiesel show a fluctuating graph. Increased total glycerol in some of the DES variations used may be due to free glycerol and glycerol bound to the biodiesel phase. Most of the DES variations used are not sufficiently capable of binding to glycerol present in biodiesel, so glycerol can not be entirely separate from the biodiesel phase (methyl ester and ethyl ester).
From Figure 3 and Figure 4 it can be seen that DES is more optimal in reducing of total glycerol with a certain concentration in biodiesel by using ethanol than methanol. And the more optimal in reducing the total glycerol is at the molar ratio of 1:2, this is because at the ratio it can be seen that the total glycerol becomes lower at few variations than that which does not use DES although the result is not constant than molar ratio of 1:3.

3.4. The Effect of DES to Ester Content of Biodiesel

Analysis of the effect of DES in the purification of biodiesel on the methyl ester content of biodiesel is done by applying different concentration of DES with different ratios and comparing it with the methyl ester content of biodiesel without DES. The methyl ester content of biodiesel without using DES is 96.836% and 95,982 for ethyl ester. Methyl ester content and ethyl ester content of biodiesel can be seen in Figure 5 and Figure 6 below:

![Figure 5](image1)

**Figure 5.** The Effect of DES to Ester Content of Biodiesel at DES Molar Ratio of 1:2

![Figure 6](image2)

**Figure 6.** The Effect of DES to Ester Content of Biodiesel at DES Molar Ratio of 1:3

In Figure 5. above can be seen that the resulting graph fluctuates. Same as the Figure 6, ester content of biodiesel show a fluctuating graph.

The transesterification reaction using DES occurs a heterogeneous reaction and then turns into a homogeneous reaction due to emulsification that can easily induce saponification. However, his reaction can be maintained as two phases with the help of DES. Since the ester is insoluble in the DES/methanol mixture, the direct contact between the ester and catalyst is significantly reduced and the ester becomes a single phase. As a result, saponification side reactions can be effectively minimized and the process of separation and purification becomes easier. Conversely, when no DES is added, the soluble ester and catalyst (at least slightly for the catalyst) in the alcohol induces
saponification, decreases the ester yield and complicates the separation and purification procedures. In addition, DES can capture side glycerol from the reactant mixture during the reaction, which shifts the reaction equilibrium to the product side and increases the ester yield. However, too much DES concentration can reduce the ester yield because the excess glycerol molecule in DES tends to bind methanol molecules which results in few free methanol molecules for the reaction and thus inhibits the reaction [11].

From Figure 5 and Figure 6 it can be seen that at the same DES concentration produces different purity ester content on each type of biodiesel. The use of ethyl ester looks more optimal in increasing the purity of ester content than methyl ester. And at different ratios it can be seen that the DES molar ratio of 1:2 is more optimal than the DES molar ratio of 1:3.

3.5. The Effect of DES to Yield of Biodiesel

While yield without using DES of 85.77% for methyl ester and 84.46% for ethyl ester. Yield with DES can be seen in Figure 7 and Figure 8 below:

![Figure 7. The Effect of DES to Yield of Biodiesel at DES Molar Ratio of 1:2](image1)

![Figure 8. The Effect of DES to Yield of Biodiesel at DES Molar Ratio of 1:3](image2)

From Figure 7 and Figure 8 it can be seen that the resulting yields ranging from 82.19 to 89.51% can be achieved with different molar ratios and concentration of DES.

From Figure 7 and Figure 8 it can be seen that at the same DES concentration produces different yield on each type of biodiesel. The use of ethyl ester looks more optimal in increasing the yield of biodiesel than methyl ester. And at different ratios it can be seen that the DES molar ratio of 1:3 is more optimal than the DES molar ratio of 1:2.
In some of the DES used, the higher of methyl ester and ethyl ester, do not guarantee the higher yield of biodiesel produced. The biodiesel yield can be affected by several factors, i.e. separation time, leaching and drying of biodiesel. In this study, the time of separation and washing was done uniformly. So, the most likely factor affecting yield is on the biodiesel drying process after the biodiesel washing process to remove remaining water content in biodiesel after washing process. This is because the time spent varies, depending on the emulsion remaining in biodiesel.

Common standards used for biodiesel quality are influenced by several factors, which differ from region to region, including the characteristics of existing diesel fuel, the type of diesel engine used, the emissions regulations for machinery, the development and climatic conditions of the country or region where production.

From the study that has been done, obtained the test results of several characteristics of biodiesel has met the Indonesian National Standard of 7182-2015 and ASTM D6751 Standard. This demonstrates the use of DES based choline chloride:1,2-propanediol as a solvent in the purification process of biodiesel by a transesterification reaction using methanol and a KOH as catalyst can provide an advantage, yielding satisfactory results and not reducing the quality of synthesized biodiesel such as density, kinematic viscosity, acid number, total glycerol and ester content.

4. Conclusion
The use of DES in the biodiesel purification process is considered good enough to increase the purity of ester content and biodiesel yield. The best DES in increasing ester content is at DES concentration of 5% with molar ratio of 1:2 for both types of biodiesel that is used is 98.089% (methyl ester) and 98.880% (ethyl ester). But on the other hand, the acid number and total glycerol of biodiesel have increased when adding DES to certain concentrations and molar ratios, so it needs to be further studied to reduce the acid number and total glycerol of the biodiesel. Overall, DES is more efficiently used in biodiesel by using ethanol (ethyl ester) than by using methanol (methyl esters).

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