

Palm ethyl ester purification by using *Choline Chloride* – 1,2 propanediol as deep eutectic solvent

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Abstract. Deep eutectic solvent (DES) has gained more attention for using in biodiesel production because of environmental benefits and process improvements. 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. The method used in preparing DES synthesis process was conducted by mixing choline chloride: 1,2-propanediol with mole ratio variation such as: 1:2 ; 1:2.5 ; 1:3 ; and 1:3.5 (mole/mole). The temperature of DES synthesis was at 80 °C with 300 rpm stirring speed for 60 minutes. Variation of DES concentration base on percentage palm oil used: 1, 3, and 5 %. DES possible to increase the ethyl ester yield of biodiesel in the purification process. The best result of yield was 89.95% with the 9:1 molar ratio ethanol: oil and 5% of DES. The operation condition was at 70 °C of temperature reaction, 400 rpm of stirring speed, and 90 minutes of reaction time.

1. Introduction

Indonesia has the highest level of fuel consumption as a source of energy. The data show that oil consumption in Indonesia reached 363.52 million BOE (Barrel of Oil Equivalent), this figure is close to 36.41% of total energy consumption of 998.53 million BOE (Barrel of Oil Equivalent) [1]. Because energy is one of the important elements in human life, there is an increase in the consumption of fuel oil as a source of energy. Human population and industrial growth will also increase energy consumption. Fossil fuels are a non-renewable fuel and are limited in nature. Continuous use of fossil fuels will lead to a fuel crisis. Currently, Indonesia has developed various alternative energy sources as a substitute for fuel oil to solve the energy crisis problem that occurred. One of them is biodiesel, is mostly produced by a transesterification reaction, from oil with an alcohol and the presence of a catalyst to generate mono-alkyl esters and glycerol, which are then separated and purified [2]. Biodiesel is an alternative fuel can use as a substitute for fossil fuels by reacting oil and alcohol. When ethanol use for transesterification, the product is FAEE (Fatty Acid Ethyl Ester).

However, 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 [3]. The resulting ethyl ester has advantages over the methyl esters, i.e., higher oxidation stability, lower iodine number, and better lubricity properties, ethyl ester also has a lower cloud point and pour point, which can increase engine life at temperature low, and a carbon atom in the ethanol molecule slightly increases combustion heat and cetane number, the studies performed show the emissions [4].



Development of low-cost and environmentally friendly solvents, known as Deep Eutectic Solvent (DES) is attractive because DES have several advantages over conventional ionic liquid and the organic solvents such easy preparation, low cost, low toxicity, and high biodegradability [5]. Recent studies had demonstrated the use of DES as co-solvent and catalyst in *methanolysis* can increase yield and make the purification easier [3]. Few studies reported the use of *ChCl* based DES with palm oil examples are the removal of an alkaline transesterification catalyst such as potassium hydroxide (KOH) and the separation of glycerol from biodiesel [6].

2. Material and Methods

2.1 Synthesis of DES

This study used a DES-based *ChCl* as ammonium salt and 1,2-propanediol as HBD. The synthesis of deep eutectic solvents (DES) performed with a fixed variable of 400 rpm stirring rate with a reaction temperature of 80 ° C for 2 hours [7] and the free variable was the molar ratio of *ChCl*: 1,2-propanediol 2: 1; 1.5: 1; 1: 1; 1: 1.5; 1: 2; 1: 2.5; 1: 3 and 1: 3.5.

2.2 Preparation of Biodiesel

The raw material used is crude palm oil and carried out pretreatment such as degumming with phosphoric acid. The result of this process is the degummed palm oil used for biodiesel production process. The transesterification reaction for biodiesel synthesis was carried out with a fixed variable of 400 rpm stirring at 70 ° C for 1 hour with a molar ratio of ethanol: DPO of 9: 1 and a catalyst concentration of 1.2% [2] and an independent variable of DES (1 , 3, 5%) and molar ratio of *ChCl*: 1,2-propanediol (1: 2; 1: 2.5; 1: 3 and 1: 3.5). In the biodiesel purification process, DES with a concentration is mixed into raw biodiesel and stirred for 5 minutes at 400 rpm.

2.3 Products Analysis

Analysis of the resulting biodiesel, Acid Numbers (AOCS Cd 3d-63 or SNI 7182-2015), Soap Numbers (AOCS Cd 3-25 or SNI 7182-2015), Total Glycerol (AOCS Ca 14-56 or SNI 7182 -2015) and analysis of ethyl ester content by using Gas Chromatography instrument (Type 122-5711, Durabond-5HT).

3. Result and Discussions

DES was use in this study were made from a mixture of choline chloride (*ChCl*) as quarternary ammonium salt and 1,2-propanediol ($C_3H_8O_2$) as Hydrogen Bond Donor (HBD) at different molar ratios. DES produced can be described in table 1 below.

Table 1. Encoding and Form of *Chcl* Based DES: 1,2-Propanediol

Molar Ratio <i>ChCl</i> : 1,2-Propanediol	Code	DES form (Room Temperature)
2.0:1	DES 1	Turbid White Solid
1.5:1	DES 2	Turbid White Solid
1:1.0	DES 3	Turbid White Solid with some Liquid
1:1.5	DES 4	Turbid White Solid with some Liquid
1:2.0	DES 5	Colorless Liquid
1:2.5	DES 6	Colorless Liquid
1:3.0	DES 7	Colorless Liquid
1:3.5	DES 8	Colorless Liquid

From table 1 above it can be seen that DES at molar ratio of 2: 1; 1.5: 1; 1: 1 and 1.5: 1 (DES 1, DES 2, DES 3 and DES 4) are not produced as good DES as solvents because of the ratio, the

resulting product forms crystals or freezes throughout the process and after cooling to room temperature.

3.1 Effect of DES on Biodiesel Acid Numbers

Analysis of the effect of DES in the purification of biodiesel on the acid number of biodiesel is done by applying different amounts of DES with different ratios and comparing it with the acid number of biodiesel without DES. The value of the the acid number of biodiesel produced without DES is 0.00165 mg KOH / g oil. By using DES, the value of acid number of biodiesel can be see in the following figure.

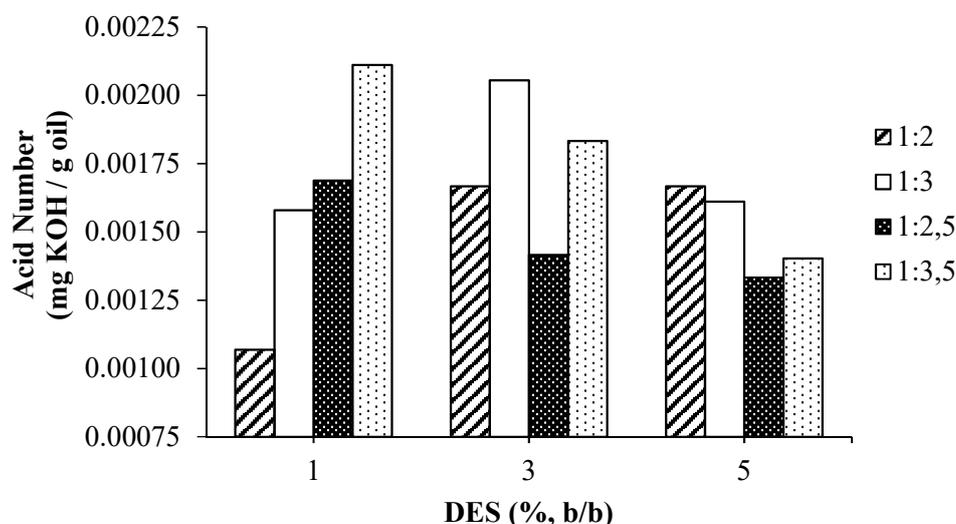


Figure 1. Effect of Total DES (%) on Acid Number of Ethyl Ester Biodiesel

From Figure1 it can be seen that at different molar ratios with the same amount of DES, acid numbers are fluctuating, except of 1% DES tends to increase as the molar increase of 1.2-propanediol HBD. In the 1: 2 molar ratio and 1: 3 the acid value increases when the addition of DES 3% and then decreases in the addition of 5% DES. In the 1: 2.5 molar ratio and 1: 3.5 the value of the acid number low with the addition of DES percent. The lowest acid number is at a 1: 2 molar ratio with 1% DES amount, while the highest acid number obtained at 1: 3.5 molar ratio with 1% DES amount.

Increasing acid numbers in some DES variations may be due to the pH of the DES it self (ChCl or 1.2-propanediol), such as ChCl having an acidic (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.

The acid number is the amount of KOH (mg) required to neutralize the free acid in the sample weight used. High acid numbers indicate the presence of oxidation reactions that occur. Because the peroxide compounds from the oxidation of oxidized unsaturated fatty acids form aldehyde compounds. The aldehydes will oxidize further to form carboxylic acids. The acid number is an important parameter as one of the indices of biodiesel quality. Because acidic numbers are potentially corrosive to vehicle engines, this is due to the high oxidation process [8].

3.2 Effect of DES on "Total Glycerol" Biodiesel

Analysis of the effect of DES in the purification of biodiesel to *total glycerol* biodiesel is done by applying different amounts of DES with different ratios and comparing it with *total glycerol* biodiesel without DES. *Total glycerol* of biodiesel produced without using DES is 0.2898%. Total glycerol of biodiesel can be see in the following figure 2.

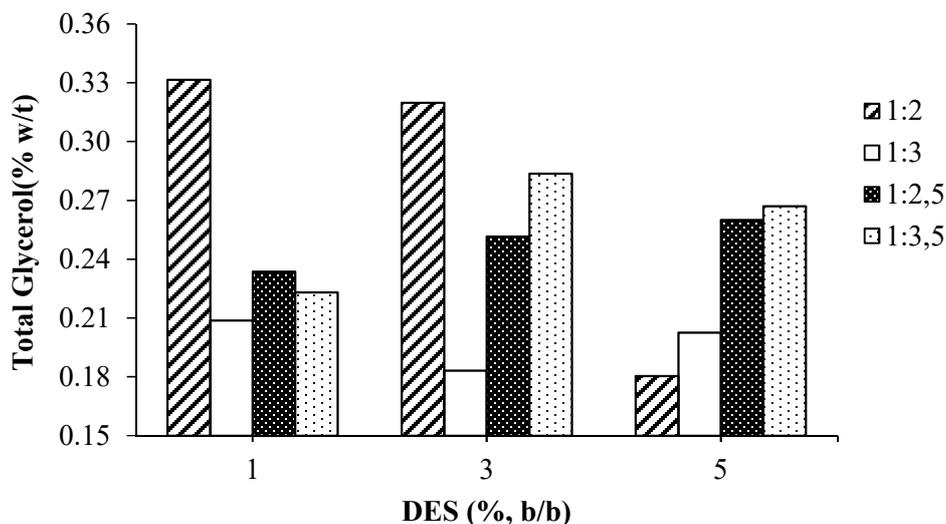


Figure 2. Effect of Total DES (%) on *Total Glycerol* Ethyl Ester Biodiesel

From Figure 2 it can be seen that between the amount of DES with *total glycerol* of biodiesel with some molar ratio has fluctuated, except in DES 5% which increases as the molar ratio of HBD increases. At a 1: 2 molar ratio the *total glycerol* value decreases with DES, whereas in the molar ratio of 1: 2.5 the decrease often increases the number of DES. The lowest *total glycerol* was at a 1: 3 molar ratio with 3% DES, while the highest total glycerol obtained at a 1: 2 molar ratio with 1% DES amount.

At the molar ratio of ChCl: 1.2 propanediol of 1: 3 are the physical properties of chemical DES produced is good. It means DES characteristics affecting the performance of solvent used in the separation of glycerol, which can be see from the *total glycerol* can be separated. The best *total glycerol* content is the lowest of 0.18%. This value obtained by the use of ChCl-based DES: 1.2 propanediol at a 1: 3 molar ratio. It shows the type of DES CHCl: 1.2 propanediol with a molar ratio of 1: 3 is the most appropriate solvent for the separation of ethyl esters of glycerol from biodiesel palm.

3.3 Effect of DES on Purity of Biodiesel

Determination of purity of biodiesel is done by standard quality analysis method for calculation of purity of biodiesel (level of ethyl ester). The method was done manually by method for titration and calculation by finding the acid number, saponification number and total glycerol of biodiesel, after which tested some result of biodiesel with Gas Chromatography as comparison. The purity data of ethyl ester biodiesel can be seen in Figure 3.

From Figure 3 can be seen that the purity of biodiesel produced using without using DES, obtained purity of 95.982% biodiesel. In the mole ratio of 1: 2 with the addition of DES of 1, 3 and 5% yielded purity of biodiesel respectively of 96.853; 96.875; And 98.880%. At a mole ratio of 1: 3 the resulting purity of 97.945 each; 98.001; And 97.790%. At a ratio of 1: 2.5 the resulting purity is 97.574; 97.414; And 96.804%. And at a mole ratio of 1: 3.5 the resulting purity is 85.88; 88.35; And 87.43%.

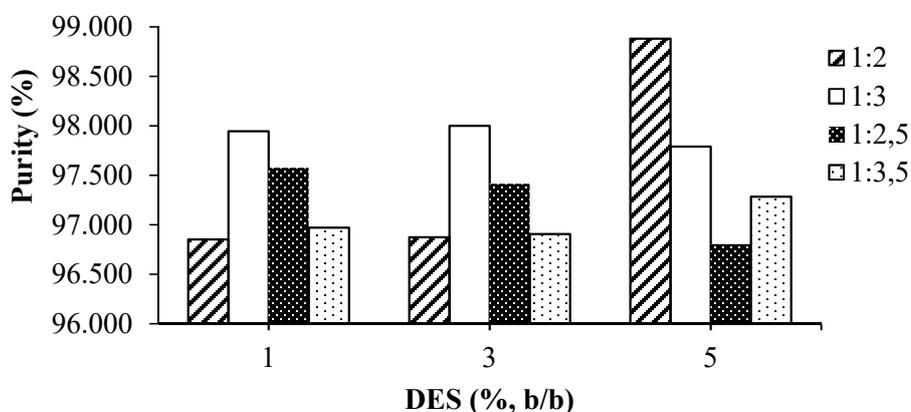


Figure 3. Effect of Total DES (%) on Ethyl Ester Biodiesel Purity

Testing by using Gas Chromatography instrument there is one sample, that is DES with molar ratio 1: 3.5 as much as 3% got ethyl ester level equal to 97.18%. While the method applied in this study obtained purity of 96.905%. So that the percentage of errata is 0.287%. With such a small percentage of errata, then the method used in this study can be done.

3.4 Effect of DES on Yield of Biodiesel

Analysis of the effect of DES on biodiesel yield is done by applying the various amount of DES and comparing it with biodiesel yield without DES. Can be seen in the following picture

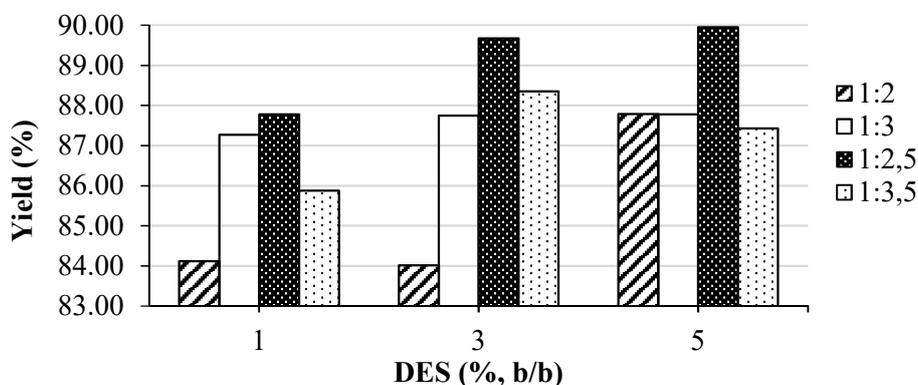


Figure 4. Effect of Number of DES (%) on Ethyl Ester Biodiesel Yield

From Figure 4 it can be seen that the yield of biodiesel produced using DES a fluctuating graph. Without using DES, obtained biodiesel yield of 84.46%. At a 1: 2-mole ratio with DES addition of 1, 3 and 5% biodiesel yields of 84.12; 84.01; And 87.78%. At a mole ratio of 1: 3 the resulting yield increases with the addition of DES. The yield of biodiesel produced was 87.27; 87.75; And 87.78%. At a ratio of 1: 2.5, yield increases along with the addition of DES. The resulting biodiesel yields were 87.78; 89.67; And 89.95%. And at a mole ratio of 1: 3.5 the yield is also increase along with the addition of DES up to 3%. Then on the addition of DES 5% biodiesel yield decreased. The yield of biodiesel produced is 85.88; 88.35; And 87.43%. The study showed that the addition of DES in amounts less than 5% (w / w) was able to increase the yield of biodiesel produced.

As shown in Figures 3 and 4, the purity of the ethyl ester biodiesel product is not directly proportional to the yield obtained. It is possible, due to the same behavior in each run of the experiment, because it should be if the resulting high purity, the yield obtained is also high.

3.5 Effect of DES on Biodiesel Washing Process

In this research, the method used in biodiesel washing process is wet washing method. After the biodiesel separation process with glycerol, biodiesel is washed with hot water to remove impurities such as alcohol residues, catalysts, glycerol which can reduce the purity and yield produced to clear water washing water.

Then also looks more turbid compared to using DES; this explains that in raw biodiesel there are still many impurities that do not separate with glycerol. Table 2. shows how much washing performed or water used for washing biodiesel From the table; it can be see that some washing of biodiesel with DES reaction with a molar ratio and a certain amount requires less water than without DES.

Table 2. Volume of Washing Biodiesel Water Conducted

Molar Ratio DES	% DES (b/b)	Volume (ml)
-	Without DES	360
	1	240
	3	230
	5	200
1:2.0	1	200
	3	250
	5	265
1:2.5	1	240
	3	250
	5	230
1:3.0	1	310
	3	300
	5	300
1:3.5	1	310
	3	300
	5	300

Many refining or washing methods have been reported to purify biodiesel. The wet washing method is the most widely used method of purifying biodiesel because only by this can reduce a number of alcohol residues and glycerol in biodiesel [9].

The table above shows the amount of washing performed or the volume of washing water used for biodiesel washing. It can be see that biodiesel washing using DES requires little washing water compared with no DES. From the above research can be concluded that by using DES can accelerate the process of separation of alkyl ester with glycerol to minimize the use of washing water and facilitate the process of purification of biodiesel.

4. Conclusion

- Choline chloride-based DES: 1.2 propanediol has the potential for biodiesel purification process to increase the purity and yield of biodiesel by 6.5%.
- The highest ethyl ester purity of 98.880% obtained at 5% DES in the DES 1: 2 mol ratio. While the yield of ethyl ester was 89.95 obtained at 5% DES amount at a mol ratio of DES 1: 2.5.
- Choline chloride-based DES: 1.2 propanediol is potentially used as co-solvent in biodiesel purification, as it can speed up the process and save up to 45% of the washing water usage.

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