Vitamin E Extraction from Red Palm Biodiesel by using K_2CO_3 based Deep Eutectic Solvent with 1,2-Propanediol as Hydrogen Bond Donor

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Keywords: Biodiesel, DES, Extraction, Vitamin E, 1,2-Propanediol.

Abstract: Deep Eutectic Solvent (DES) is the latest advancement in separation technology to extract vitamin E from its source. In this research K_2CO_3 based DES with hydrogen bond donor (HBD) of 1,2-propanediol was used to extract vitamin E from red palm biodiesel. The DES was synthesized at temperature of 80 ^oC for 1 hour by stirring rate at 300 rpm and K_2CO_3 to 1.,2-propanediol molar ratio variation of 1:7, 1:8 and 1:9. Red palm oil was synthesized by degumming of CPO with 85% phosphate acid to obtain Degummed Palm Oil (DPO). The extraction was performed by mixing between biodiesel and DES at 400 rpm for 3 hours in mass ratio of 1:2, 1:2,5. 1:3, 1:3,5 and 1:4. Based on molar ratio variation of of K_2CO_3 :1,2-Propanediol and mass ratio of biodiesel:DES, which effect to extracted vitamin E and biodiesel purity. The HPLC analysis was used to showed concentration of extracted vitamin E while the GC analysis was used to showed that extraction using K_2CO_3:1,2-propanediol based DES indeed can increase the purity. DES at K_2CO_3 to 1,2-propanediol molar ratio of 1:8 and biodiesel to DES mass ratio of 1:3.5 was the most effective in extracting vitamin E up to 392.16 ppm.

1 INTRODUCTION

Biodiesel is generally produced by transesterification reaction. The palm oil transesterification is a gradual reaction between palm oil and alcohol (methanol or ethanol) producing methyl esters or ethyl seters (Manurung, 2018a). Raw material requirements for biodiesel production is the main consideration to increase the economic value of biodiesel production where waste cooking oil, crude palm oil (CPO) can be an alternative choice that can replace the usage palm oil. In Indonesia, palm oil is a raw material that is quite potential to be used for biodiesel production because it is available throughout the year in large quantities (Manurung, 2018b). Crude palm oil is converted to methyl ester that called biodiesel and side product in the form of glycerol was obtained from the reaction between raw materials in the form of triglycerides using short chain alcohols such as methanol and ethanol assisted by the presence of alkaline catalysts. Biodiesel is ecofriendly diesel and good performance (Manurung, 2018a).

One of the most prospective raw materials in biodiesel production is obtained from palm oil. This is due to the availability of palm oil is in large amount in Indonesia, from September to October 2016, the average production of palm oil reached 35 million tons, and exports reached 26 million tons and domestic consumption of 9.1 million tons in October 2016 (World Market and Trade, 2016). Indonesia as one of the largest palm oil producer country in the world has the potential to develop palm oil-based biodiesel compared to fossil fuels.

One of minor component in CPO-based biodiesel which can also be classified as an impurity is carotenoids, and several other micronutrients such as vitamin E, tocotrienol and sitosterol (β-sitosterol) which are useful. Crude palm oil is a vegetable oil containing minor components such as carotenoids and vitamin E where the vitamin E content in the CPO is approximately (600-1000 μg/ml) (Sinaga and Donald, 2015). Among tocopherols, α-tocopherol is the most important source of vitamin E in human foods. The ability of antioxidants and their function as anti-free radicals makes tocopherols become an attractive molecule for the health and food industry.
Due to the function of tocopherol which is very important for living things, it can be encourages the

Manurung, R., Ramadhan, G., Arief, A. and Siregar, H.
Vitamin E Extraction from Red Palm Biodiesel by using K2CO3 based Deep Eutectic Solvent with 1,2-Propanediol as Hydrogen Bond Donor.
DOI: 10.5220/0010094503380345
In *Proceedings of the International Conference of Science, Technology, Engineering, Environmental and Ramification Researches (ICOSTEERR 2018) - Research in Industry 4.0*, pages 338-345
ISBN: 978-989-758-449-7

development of the separation of these compounds from the sources. Several studies have been carried out such as adsorption, membrane separation technology, and the use of solvents extraction (Bezold, 2017) (Dai, 2015).

To obtain these components from methyl esters, it is necessary to maintain the components in the palm oil methyl esters with certain techniques, it can be performed using Deep Eutectic Solvent (DES). DES is produced by mixing two components in certain ratio to produce a mixture which has significantly lower melting points than each of the components singularly. Moreover DES has lower toxicity level and most of them are biodegradable (Manurung, 2018b). As well as the usage of ChCl, in 2013, potassium carbonate (K_2CO_3) and glycerol were used in different molar ratio to create a new DES system (Manurung, 2018b).

The development of the DES system is increasingly in demand because it has been widely applied as co-solven, liquid-liquid extraction and in catalysis which can be used economically and ecofriendly properties (Dai, 2015) (Manurung, 2018b). The use of 1,2-Propanediol as HBD was carried out by (Manurung, 2018a) in the process of purifying biodiesel in which biodiesel was purified up to 99.88% (Manurung, 2018a). This research tried to synthesize DES based on K_2CO_3 with 1,2-Propanediol as HBD to purifing red palm biodiesel which expected that DES have ability to act in extracting the oil components in the form of tocopherols as vitamin E within CPO.

2 MATERIAL AND METHODS

2.1 Materials

Crude Palm Oil (CPO) was obtained from the palm oil mill (PKS) PTPN IV. Phosphoric acid (85%) was used to CPO pretreatment to obtained degummed palm oil (DPO). Biodiesel based red palm oil was conducted by ethanol (C_2H_5OH) as alcohol, potassium hydroxide (KOH) as catalyst, and aquadest used to biodiesel washing process. The DES synthesis was used potassium carbonate (K_2CO_3) based 1,2-Propanediol as HBD. The extraction process used n-hexane to disperse biodiesel and used methanol to disperse DES thus the liquid-liquid extraction could create biphasic system. Recovery of vitamin E used water-hexane method in 4:1 ratio, then concentrate was obtained by using rotary evaporator.

2.2 Methods

The synthesis of deep eutectic solvent (DES) was conducted at temperature of 80 ºC, stirring rate of 300 rpm for 1 hour (Manurung, 2018a), and molar ratio variation of K_2CO_3 to 1,2-Propanediol 1:7, 1:8 and 1:9. The transesterification reaction to synthesis biodiesel was performed at temperature of 70 ºC for 1.5 hours by molar ratio of ethanol : DPO = 9:1, and KOH concentration of 1.2 wt%. The extraction process adopts the procedure by is based on a method performed by (Manurung, 2018) (Manurung, 2018c), n-hexane was used to disperse biodiesel and methanol was used to disperse DES which then performed liquid-liquid extraction by mixing biphasic system between prepared CPO and DES. Mass ratio of Biodiesel to DES was varied at 1:2, 1:2.5, 1:3, 1:3.5 and 1:4. Recovery of vitamin E was carried out by of water-hexane method at ratio of 4:1 v/v. The concentrate was obtained by using rotary evaporator the vitamin E rich hexane product from water-hexane recovery process

3 EXPERIMENTAL PROCEDURE

3.1 Synthesis of Deep Eutectic Solvent (DES)

DES was performed by K_2CO_3 and 1,2-Propanediol with a certain molar ratio was introduced into the erlenmeyer and sealed it with stopple. The mixture is heated over hot plate until it reaches the reaction temperature of 80 °C and then stirring at 300 rpm for 1 hour to obtained homogenous mixture (Manurung, 2018c).

3.2 Pretreatment of Crude Palm Oil

Crude palm oil in certain amount was put into beaker glass. Palm oil was heated to 80 °C. 85% phosphoric acid was added as much as 0.15% of the used palm oil weight. The oil was then stirred at 300 rpm for 15 minutes. CPO was filtered using filter paper. The filtrate was taken and called by Degummed Palm Oil (DPO).

3.3 Synthesis of Biodiesel

DPO, ethanol, and KOH catalyst are prepared in a certain weight. The equipped Three-neck flask with magnetic stirrer, a thermometer, and condensation system are heated by hot plate to temperature of 75 ºC to remove water content. DPO in certain weight was added to the three-neck flask and heated to temperature of 70 ºC. Ethanol and KOH catalyst were added to the three-neck flask and turned on the magnetic stirrer, the stopwatch was run to calculate the reaction time. After 1.5 hours, the hot plate was turned off and the mixture cooled. The reaction mixture was then introduced into the separating funnel and waited for a few minutes to form 2 layers so that the separation of the mixture can be performed. The bottom layer which is a mixture of glycerol, ethanol, and KOH was separated from the top layer containing crude palm biodiesel which still contained some impurities. The top layer then washed using hot water until the bottom layer is clear to remove any remaining impurities (Manurung, 2018d).

3.4 Extraction of Vitamin E

Prepared 10 grams of biodiesel was mixed with 100 ml n-hexane. DES with a certain mass ratio to biodiesel was then mixed with 100 ml methanol. Mixed both of those two mixtures and stirred at 400 rpm for 3 hours and then let it for 2 hours in the separation funnel. The mixture will form two layers, the bottom layer which is a mixture of DES, methanol and vitamin E was then separated from the top layer.

The bottom layer mixture was then mixed with water-hexane by volume ratio of 4:1 v/v in separation funnel and let it to form 2 layers. The lower layer which is a mixture of DES, methanol and water was separated from the top layer. The top layer was condensed with rotary evaporator till there was no more hexane remaining to obtained vitamin E, so that the biodiesel purity can be analyzed (Hadi, 2014).

4 RESULTS AND DISCUSSION

4.1 Characteristic of DES

DES is produced by mixing two components in the certain ratio to produce a mixture which has significantly lower melting points than each of the components singularly (Craveiro, 2016). In this study used Potassium carbonate (K_2CO_3) and 1,2-Propanediol in different molar ratios to create a new DES system. The need development for green solvent which can be used economically and applicable not only just limited in gas absorption, liquid-liquid extraction and catalysis (Setyawan, 2011).

4.1.1 Form and Appearance of DES

The goal in this part is to obtain DES with the best characteristics as a solvent. The used DES was a mixture of K_2CO_3 and 1,2-propanediol as HBD with various molar ratios can be explained in Table 1 below.

Table 1: Code and from of K_2CO_3 based DES with 1.2 propanediol as HBD.

Ratio Molar of K_2CO_3:1.2 Propanediol	Code	Form of DES (RoomTemperature)
1 : 2	DES 1	White color, partial Solid
1 : 3	DES 2	White color, partial Solid
1 : 4	DES 3	Turbid, still there solid
1 : 5	DES 4	Turbid, still there solid
1 : 6	DES 5	Transparent, still there solid
1 : 7	DES 6	Transparent, Liquid
1 : 8	DES 7	Transparent, Liquid
1 : 9	DES 8	Transparent, Liquid

Based on Table 1 shows that DES at molar ratio of 1:2, 1:3, 1:4, 1:5 and 1:6 (DES 1, DES 2, DES 3, DES 4 and DES 5) visually were still produced poor DES. The produced product was turbid, white and freezing at room temperature. The phase of solid, semi-solid, crystal, or liquid will be formed along and after the preparation of DES synthesis with different forming phase.

Important physical properties Characterization of DES are viscosity, density, refraction index, pH, and surface tension, (Dai, 2015). In this research, the obtained DES Characterization were freezing point, density, and viscosity.

4.1.2 Freezing Point of DES

DES is usually consisted of two or three cheap and safe components, which can associate with each other through hydrogen bond donor, to produce eutectic mixture in the liquid phase when freezing point of DES is much lower than it's pure constituents. The effect of molar ratio to freezing point of DES can be explained in Figure 1 below.

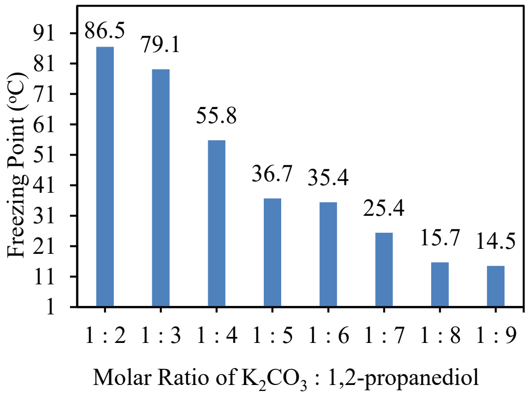

Figure 1: Molar ratio effect to DES freezing point.

Freezing point value is decreased by the increasing of DES molar ratio. Freezing point value from DES 1 until DES 8 are 86.5, 79.1, 55.8, 36.7, 35.4, 25.4, 15.7 and 14.5 ºC. Mixing ammonium quarterner salt (K_2CO_3) with hydrogen bond donor at a certain molar ratio to form eutectic mixture forms the liquid phase of DES. HBD forms a simple complex with anion salts which leads to a reduction of the lattice energy in the system and decrease of freezing point (Manurung, 2018d). So it can be stated that the suitable DES molar ratio to be used as a solvent are 1:6. 1:7 and 1:8 because these molar ratio produced DES with the lowest freezing point.

4.1.3 Freezing Point of DES

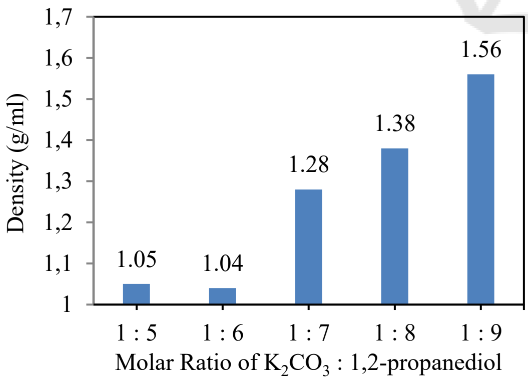

Figure 2: Molar ratio effect to DES density.

Density is one of DES important physical properties. The produced DES density also affected by different molar ratios. It was found that by the increasing of HBD mole fraction will also increase the DES density (Manurung, 2018a). Figure 2 shows that the effect of molar ratio of K_2CO_3 : 1,2-propanediol to the DES density value.

All of the DES density values were above 1.04 g/cm^3. This value lies between the density of K_2CO_3 and the density of 1,2-propanediol, where their density are 2.43 g/cm^3 and 1.040 g/cm^3 respectively. The density value of DES is higher than the density of water and density of HBD constituent.

4.1.4 Viscosity of DES

Viscosity describes the internal friction forces which occur in the moving fluid or in other words viscosity is fluid resistance to each flow. Most reports about DES show that DES has high viscosity value, usually above 100 cP. Viscosity is an important characteristic of DES (Manurung, 2018b,d). Figure 3 shows that the effect of molar ratio of K_2CO_3: 1,2-propanediol to the DES viscosity value.

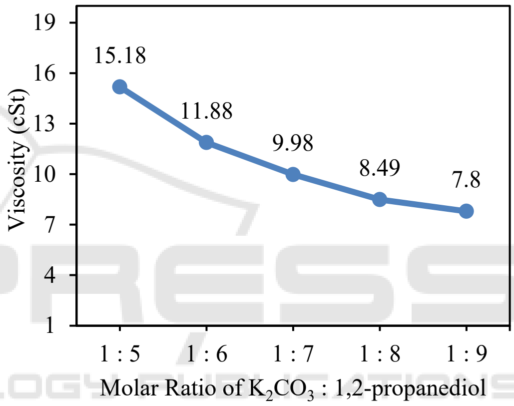

Figure 3: Molar ratio effect to DES viscosity.

Based on Figure 3 shows that the viscosity values for each DES4, DES5, DES6, DES7 and DES8 respectively are 15.18, 11.88, 9.98, 8.49 and 7.80 cSt, where obtained DES viscosity is below 100 cP at room temperature (Manurung, 2018b,d). Solid phase can be seen at molar ratio of K_2CO_3 to 1,2-Propanediol of 1:2 and 1:3. In this case can not be measured and not good choice to applicated as a green solvent.

The highest of DES viscosity is believed due to the presence of hydrogen-bonding excess between combinations that limit the movement of free bonds within the DES. Other interactions, such as Van Der Waals and electrostatic interactions, can also affect the highest viscosity in DES (Zainal, 2017).

4.2 Concentration of Vitamin E

In this part, the goal to be achieved is to know the potential and effectiveness of K_2CO_3-based DES with

1,2-propanediol as HBD usage as solvent in vitamin E extraction and biodiesel purification.

4.2.1 Pretreatment of Crude Palm Oil

The purpose of this part is to know the quality of the used raw material in transesterification process to produce biodiesel. The used raw material was Crude Palm Oil (CPO), the compositions of used CPO fatty acid are known from Gas Chromatography analysis (Type 122-5711, Durabond-5HT; Length = 15 m, inner diameter = 0.250 mm, film = 0.10 µm) with a molecular weight of FFA is 271.8016 g/mol, while the molecular weight of CPO (in the form of triglycerides) is 853.4571 g/mol. From the analysis of Gas Chromatography instrument, the composition of CPO saturated fatty acids is 42.12%, while the unsaturated fatty acid is 57.88% as shown in Table 2.

Biodiesel production that uses CPO as raw materials is generally carried out by degumming process at first. This step is the process of separating unwanted gum which can usually interfere with the stability of the oil at the next step. Degumming can be done by treating CPO with phosphoric acid or citric acid at certain concentrations (Manurung, 2018b), while in this research using phosphoric acid 85%.

Degumming acid with phosphoric acid is intended to separate phosphatida which is a source of unwanted taste and color. Gum contained in CPO may block the activity of catalysts to accelerate reaction equilibrium. Used DPO as raw material can expected the purity and yield come to be higher Manrung, 2018a,b).

4.2.2 Free Fatty Acid

Comparison of free fatty acid (FFA) levels of crude palm oil (CPO) and degummed palm oil (DPO) is presented in Figure 4. From Figure 4 it can be seen that the FFA level in DPO is higher than FFA level in CPO. FFA level in CPO is 4.52%, while the FFA level in DPO is 4.77%. The increase of FFA level in CPO after degumming process is 0.19%. This increase in FFA level indicates a decrease in most gum and impurities which can inhibit catalyst activity and affects the produced product.

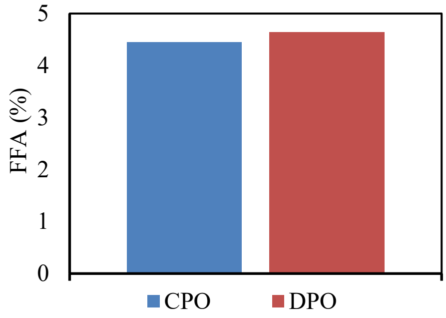

Figure 4: Analysis of FFA content in CPO and DPO.

Based on Figure 4 it can be seen that there is an increase in FFA levels after degumming although not significant. It is caused by the use of phosphoric acid capable of hydrolyzing oil or trigliserida in the presence of heat application (Manurung, 2018a, b). To produce biodiesel, it is important to keep FFA levels less than 6% to prevent unwanted saponification reactions due to the presence of free fatty acids that react with alkaline. In the presence of highest FFA levels can reduce the yield of biodiesel.

4.3 Extraction of Vitamin E

The determination of extracted vitamin E content from red palm biodiesel using instrument analysis. The analytical instrument used to test the

Table 2: Compositions of fatty acid in CPO (Crude Palm Oil).

No.	Retention Time (minute)	Compounds	Composition (%) (w/w)
1	10.357	Lauric Acid ($C_{12:0}$)	0.08
2	12.794	Miristic Acid ($C_{14:0}$)	0.61
3	15.213	Palmitic Acid ($C_{16:0}$)	36.37
4	15.464	Palmitoleic Acid ($C_{16:1}$)	0.11
5	17.568	Stearic Acid ($C_{18:0}$)	4.78
6	17.764	Oleic Acid($C_{18:1}$)	43.01
7	18.194	Linoleic Acid ($C_{18:2}$)	14.49
8	18.760	Linolenic Acid ($C_{18:3}$)	0.19
9	19.826	Arachidic Acid ($C_{20:0}$)	0.28
10	20.023	Eikoseneic Acid ($C_{20:1}$)	0.08

concentration of extracted vitamin E is High Performance Liquid Chromatography (HPLC).

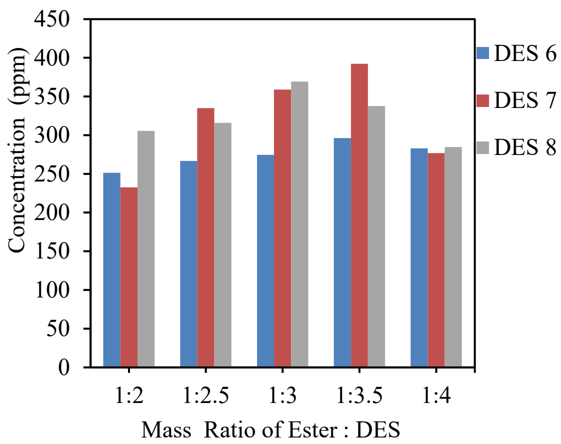

Figure 5: Concentration of extracted vitamin E vs ratio of biodiesel : DES.

Figure 5 shows an increased in extracted vitamin E concentration by the DES6, DES7 and DES8 until mass ratio of 1:3.5 and continued to decrease by usage of DES with biodiesel to DES mass ratio of 1:4 and at that point DES6, DES7 and DES8 reached the lowest concentration of vitamin E which can be extracted by K2CO3 based DES with 1,2-propanediol as HBD.

Vitamin E concentration which can be extracted by DES6 with biodiesel to DES mass ratio of 1:2, 1:2.5, 1:3, 1:3.5 and 1:4 respectively are 251.30, 266.62, 274.44, 296.23 and 282.87 ppm, by DES 7 with biodiesel to DES mass ratio of 1:2, 1:2.5, 1:3, 1:3.5 and 1:4 respectively are 232.62, 334.87, 358.80, 392.16 and 276.87 ppm and by DES8 with biodiesel to DES mass ratio of 1:2, 1:2.5, 1:3, 1:3.5 and 1:4 respectively are 305.47, 315.75, 369.19, 337.19 and 248.61 ppm.

The polarity of the DES is an important factor in determining separation efficiency which is influenced by the interactions between the solute (vitamin E) and the DES. In this research used water to get vitamin E concentrate from DES-methanol by using water-hexane method in the volume ratio of 4:1 v/v in the funnel separation. The result in this research is fit with the conducted study by (Dai, 2015). DES containing high percentage of water will result in high yield at polar bond, while DES containing low percentage of water will result in low yield at non-polar bond in the water-hexane system to recover vitamin E. So the usage of water is to bind DES and release Vitamin E from DES into n-hexane (Setyawa, 2011) (Tang, 2015).

The highest concentration of extracted vitamin E from biodiesel using K_2CO_3 based DES with 1,2-Propanediol as HBD is resulted by DES 7. Extraction using DES 6 and DES 7 resulted the highest concentration of extracted vitamin E by biodiesel to DES mass ratio of :3.5 at 296.23 ppm and 392.16 ppm, While on DES 8, the concentration of vitamin E at biodiesel to DES mass ratio of 1:3 is 369.19 ppm. This shows that the extraction process using K_2CO_3-based DES with 1,2-propanediol as HBD can ended extract vitamin E from palm biodiesel under certain conditions.

4.4 Purity of Biodiesel

Purity of biodiesel is determined by the ester content in produced biodiesel. Determination of ester content from red palm biodiesel used Gas Chromatography (GC) instrument. Figure 6 shows the effect of Biodiesel : DES mass ratio to ester content.

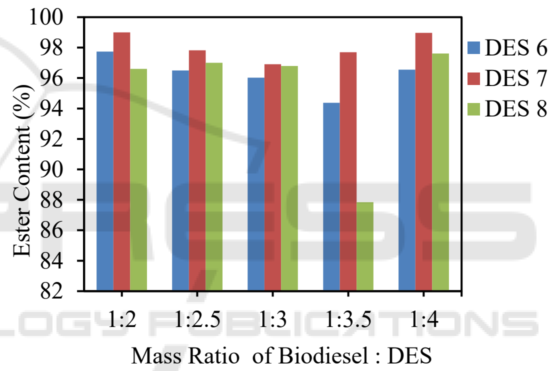

Figure 6: Ester content (%) vs. mass ratio of biodiesel: DES.

The resulted ester content by DES6 at biodiesel : DES mass ratio of 1:2, 1:2.5, 1:3, 1:3.5 and 1:4 respectively are 97.74%, 96.5%, 96.02%, 94.38% and 96.55% , by DES7 at biodiesel to DES mass ratio of 1:2, 1:2.5, 1:3, 1:3.5 and 1:4 respectively are 99.01%, 97.83%, 96.91%, 97.69% and 98.97% and by DES 8 at biodiesel to DES mass ratio of 1:2, 1:2.5, 1:3, 1:3.5 and 1:4 respectively are 96.60%, 97.01%, 96.79%, 87.85% and 97.61%. The higher ester content in biodiesel means the higher purity of biodiesel. The purity of biodiesel before extraction and after extraction can be compared in Figure 7 below.

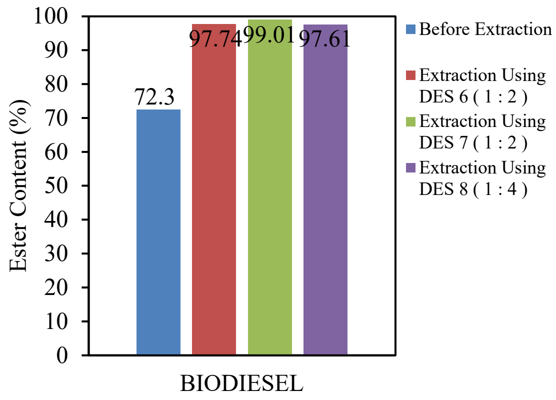

Figure 7: Comparison of biodiesel purity before and after extraction.

Biodiesel has presence of emulsions or major impurities such as glycerol, catalyst, alcohol, triglycerides, diglycerides and monoglyaccharides and minor impuritives such as carotenoids, vitamin E, tootrienol and sitosterol (β-sitosterol) (Hamilton, 1995) will affect the purity of the esters produced. One of minor component in biodiesel that is the trapped vitamin E, because Vitamin E (tocopherol) is an antioxidant that is non-polar (hydrophobic) (Khanum and Thevanayagam, 2017). Besides that ethyl ester is a compound that has a long carbon chain that is also hydrophobic (Hadi, 2014), then large amounts of vitamin E will be bound to ethyl esters which are both non-polar and stable. In the process of refining biodiesel with washing method using water is not enough to increase the purity of palm biodiesel. So it takes a solvent like DES in the purification process to bind vitamin E and increase the purity of palm biodiesel.

It can be seen that the purity of biodiesel before it was extracted by potassium carbonate based DES with glycerol as HBD, the obtained ester content was 72.53%, the low purity of produced ethyl ester is due to contaminant component which is not efficiently washed by water. Compared to the biodiesel after extraction using K_2CO_3 based DES with glycerol as HBD where the purity of produced biodiesel increased untill above 96.5% averagely, although there were some results which have under the avarage purity value but Figure 7 shows that K_2CO_3 based DES with glycerol as HBD not only able to extract vitamin E but also can improve purify of the palm ethyl ester into high purity as a biodiesel. The addition of DES in amounts less than 5% (w/w) was able to increase the yield of biodiesel produced (Manurung, 2018c).

5 CONCLUSIONS

K_2CO_3 based DES with 1.2-propanediol as HBD which has god characteristics as solvent was obtained by K_2CO_3 to glycerol molar ratio of 1:7, 1:8 and 1:9 based on the characteristics of freezing point, density, and viscosity. The used CPO had 4.52% concentration of free fatty acid (FFA) and after pretreatment process the concentration of FFA increased to 4.77%. DES8 with K_2CO_3 to 1.2-propanediol molar ratio of 1:8 was the most effective DES in extracting vitamin E from palm biodiesel with biodiesel to DES mass ratio of 1:3.5 by vitamin E concentration of 392.16 ppm. The highest palm biodiesel purification ability was performed by using DES8 with K_2CO_3 to 1.2-propanediol molar ratio of 1:8 at biodiesel to DES mass ratio of 1: 2 resulted biodiesel purity of 99.01%.

ACKNOWLEDGEMENTS

The authors are grateful to DRPM DIKTI which has accomodated the authors in completing this paper.

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