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Separation of Tocopherol from Crude Palm Oil Biodiesel

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ABSTRACT

A molecular distillation procedure was developed to extract tocopherols from crude palm oil based biodiesel. Change of CPO to biodiesel can be made by esterification and transesterification reaction. Use of esterification and trans-esterification reaction were facilitated the process of molecular distillation because of the heavy molecules such as glycerol have been separated first. The conditions of molecular distillation to recover tocopherols were set-up of with a flow rate of 1.3 liter/jam-1, 7 liters / hour, distillation temperature 175 ˚ C - 220 ˚ C and 200 rpm rotational speed wipers - 400 rpm. It was found that the yield of tocopherols were the separated between 22.9 mg - 605 mg from 1.302 mg of overall tocopherol content in crude palm oil based biodiesel. The overall recovery of tocopherols was around 35% of the original content in crude palm oil based biodiesel. In the residue, there were no different value in acid number, FFA content, density, kinematic viscosity and iodine value of crude palm oil based biodiesel after molecular distillation process.

KEY WORDS: crude palm oil based biodiesel; tocopherol; molecular distillation.

INTRODUCTION

Crude palm oil (CPO) has major components in the form of triglycerides, free fatty acids, diglycerides, and minor components such as mono-alkyl-glycerol, sterols, glycolipid, phospholipids, squalled, carotenoids, hydrocarbons and triterpene alcohol (Ketaren, 2005). According to May (2007) CPO containing 1% minor components consisting of carotene, vitamin E (tocopherol and tocotrienol), sterols, phospholipids, glycolipid, terpene and hydrocarbons. Tocopherol and tocotrienol concentration is about 600 - 1000 ppm in CPO.

Tocopherol has the highest antioxidant activity of vitamin E other members. Therefore, isolates of tocopherol can be used as additives to improve the content of vitamin E in foods. Usability tocopherol is an antioxidant. Tocopherol and tocotrienol will absorb free radicals and react to form harmless compounds that can be absorbed by other antioxidants.

Potential tocopherol utilization was much to encourage the development of separation technology of tocopherol. There are several kinds of tocopherol separation technology, such as separation using membrane technology, adsorption, and extraction with a solvent. Several studies of tocopherol isolation using molecular distillation has been carried out with the raw material palm fatty acid distillates (PFAD) (Posada et al. 2007) and rapeseed oil Deodorizer distillate (Rodd) (Shimada et.al. 200) and (Shao et al. 2007).

Tocopherol separation of CPO can be done by molecular distillation by changing the CPO to biodiesel first. Change of CPO to biodiesel can be made by esterification and transesterification reaction. Use of esterification and transesterification reaction are facilitated the process of molecular distillation because of the heavy molecules such as glycerol have been separated first. Batistella (1998) had use esterification and transesterification reaction as pretreatment to separate the carotenoids from palm oil by molecular distillation. The purpose of this study was to obtain tocopherol rich fraction of palm oil biodiesel with molecular distillation and get results CPO biodiesel quality analysis after separation process.

Molecular distillation is a separation process fraction of different molecular weights at temperatures as low as possible to avoid damage. The advantage of using molecular distillation technique is the separation process under vacuum so that the temperature of the separation can be kept to the minimum possible to avoid damage to materials

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(Shao et al. 2007). The use of molecular distillation to separate the tocopherol-rich fraction of palm oil biodiesel and biodiesel are expected not to damage resulting tocopherol, obtained a high recovery, and the stage of the process is relatively short.

MATERIALS AND METHODS

Material

The materials used in this study is crude palm oil coming from PT Perkebunan Nusantara VIII Malimping Serang Banten Indonesia, alpha-tocopherol standards (Sigma-Aldrich T3251-56, Synthetic, 95% HPLC), HPLC grade hexane, HPLC grade isopropanol, methanol, NaOH, sulfuric acid, KOH, PP and other chemicals.

The equipment needed are a molecular distillation turnkey production manifold Pope Science, 6", Two-Stage Pilot Plant Molecular Still, with specifications of 0.22 m^2 of body area of stainless steel, material flow rate between 2 to 50 liters / hour, vacuum pressure from 300 torr to 5x10-3 torr, with operable distillation temperature ranging from 0-400°C (Pope Science, 2008), esterification and transesterification reactor, High Performance Liquid Chromatrography (HPLC) Zorbax SIL column (0.46 x 25 cm) with mobile phase of isopropanol: heksane (0.5: 99.5 v / v) for absorbance α tocopherol (Tay et al. 2002).

Method

In the process of making biodiesel, crude palm oil as much as 1000 ml heated to 55°C temperature, methanol plus 225% of the total FFA and sulfuric acid catalyst 5% FFA. Then the mixing was stirred 350 rpm to ensure a uniform temperature and the suspension to form esters. Mixture temperature is maintained at 55°C for 1 hour. After the reaction is complete, the trans-esterification reaction is done by adding 15% methanol and NaOH in increments of 1% of the amount of oil. Stirring was continued for 1 hour until a brownish color that has marked the formation of glycerol as a side product.

Methyl esters and glycerol are separated using a separator flask. The bottom layer is the glycerol and methyl ester at the top. Methyl ester is separated and washed with distilled water temperature 50°C to remove any residual catalyst, methanol and soap, up to three times of washing. Drying methyl esters or biodiesel is used the heating temperature of 115°C until all the water evaporates.

Biodiesel produced was analyzed the physical and chemical properties.

The conditions of molecular distillation to recover tocopherols were set-up of 1.3 liter / h of feed flow rate, evaporating temperature of 218 ° C and wiper rolling speed of 400 rpm (Lutisan, et.al. 2001).

RESULTS AND DISCUSSIONS

a. Tocopherol Content of Biodiesel CPO

The content of tocopherol in palm oil biodiesel were analyzed. Each treatment is using palm oil biodiesel raw materials as much as 2 liters (2000 ml). Result analysis shown that tocopherol concentration in CPO biodiesel is 651 (g / ml). Therefore, the amount of tocopherol in palm oil biodiesel is 1,302,000 g, or 1302 mg or 1.3 grams per 2 liters of palm oil biodiesel.

b. Separation Results

Based on the calculation of molecular weight, molecular weight of palmitic metyl ester according to Jiang et.al (2006) is 270.2559 [g / mol] while the molecular weight of tocopherol is 430.7061 [g / mol] (Pumchem 2008). Distillation process starts with evaporating molecules with molecular weight of more mild to severe. The research data obtained by analyzing the concentration of tocopherol contained in the distillate. According to Posada (2007), tocotrienol with tocopherol will be separated and entered into the distillate at high temperatures. Tocopherol remains with the residue if the material is distilled under 115 ° C, while the best results for minor components of palm oil distillation is achieved at temperatures above 160 ° C. At temperatures above 160 ° C tocopherol will evaporate and enter the distillate (Posada 2007). In this study, the temperature of distillation begins at a temperature of 175 ° C, so that most terdistilasi tocopherol and accumulates in the distillate. Temperature treatment in this study begins at 175 ° C because preliminary research based, began to produce phase distillate distillation at a temperature of 170 ° C.

Based on the calculation of the amount of tocopherol that separated, it can be seen that the lowest amount of tocopherols which can be separated by using molecular distillation as much as 22.9 mg found on treatment with a flow rate of 2 liters / hour, distillation temperature of 159.9 ° C and rotation speed wipers 300 rpm). The highest tocopherol contained 605 mg of treatment with a flow rate of 1.3 L / h, distillation temperature of 220 ° C and a wiper speed of 200 rpm.

Decrease tocopherol recovery in line with the increased flow rate. Tocopherol more often found in distillate at the lowest flow rate. This is related to waiting time (retention time) tocopherol in the evaporator. At low flow rate, the energy molecule (tocopherol and tocotrienol) have enough time to reach the surface of the solution, therefore these molecules can exit onto phase terdistilasi (Posada 2007).

The significance of the influence of a low flow rate in this study shows the amount of flow rate influence on waiting time (retention time) methyl ester in the evaporator. That is, flow rate of 2.7 liter per hour as the highest fuel flow rate has a much different retention time with a flow rate of 1.3. Although the tools used are different, especially on cross-sectional area of evaporation and flow rate, recovery profiles tended to the same result. Sectional area of evaporator on Posada (2007) is 0.043 m2, whereas in this research area is smaller evaporation 0.022 m2. Material flow rate on Posada (2007) from 0.1 Kg / h - 0.4 Kg / h is much smaller than the material flow rate in this study that reached 2.7 Liter / hour.

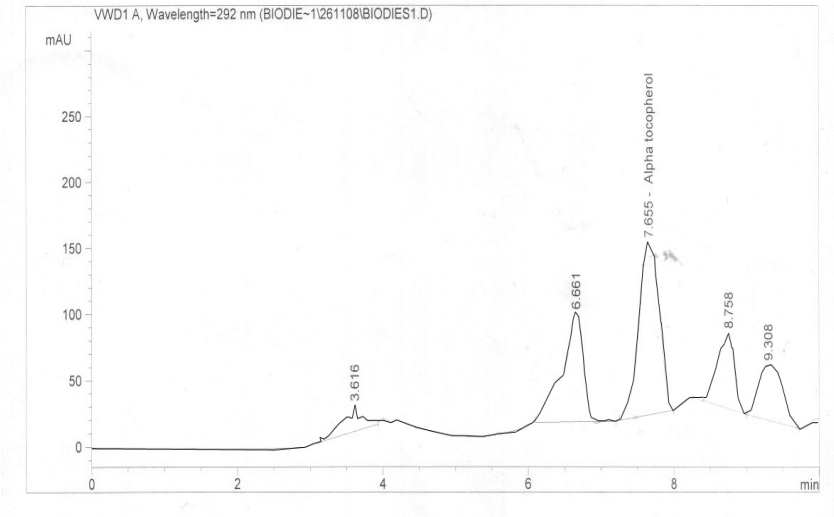

Figure 1. Tocopherol Analysis using HPLC

Improved recovery of tocopherol at higher temperatures shows that distillation temperature influence on the model. According to Posada (2007), the higher the temperature of distillation, the more components that go into phase distillate. Based on Posada (2007), distillation temperature below 120 ° C will be able to separate the FFA and squalen, whereas tocopherol and tocotrienol begin to separate at temperatures above 160 ° C.

Wiper rotation difference has less affect the results of tocopherol recovery. Wiper function is essentially to facilitate the process of distillation evenly both at the surface of the wall of the internal heating and controlling the thickness of the thin layer / layer of raw material on the wall. Various kinds of wiper speed is used to obtain supplies of raw materials in the most efficient on the surface of the distillation and maintain a stable surface. A thin layer of material becomes unstable (noise) when the wiper rotates too fast (Jiang, 2006).

c. Physical and Chemical Analysis of Biodiesel Before and After Molecular Distillation Process

Molecular distillation produced two fractions, the residue and distillate. The residue is a material that does not vapour, while distillate is the result of distillation. This study was originally intended purpose is to separate the tocopherol-rich fraction of palm oil as biodiesel feedstock.

Based on research result, it shows that the tocopherol-rich fraction contained in the distillate. This indicates that the residue is a methyl ester which does not distillated. According to the Indonesian Biodiesel SNI Hambali (2006), methyl esters can be 90% distillated at temperature of 360 ° C. The highest temperature in this study is 220 ° C, so that residues much dominated by the methyl ester.

Table 1. Biodiesel Quality Comparison Before and After Molecular Distillation

Quality Parameters	Biodiesel Before Distillation Process	Biodiesel After Distillation Process	Standard Biodiesel Indonesia
Iodine number	59.7	55.4	<115
Free Fatty Acid (%)	0.4	0.48	<0.8
Density (g/cm2)	0.8696	0.8690	0.86 – 0.88
Kinematic viscosity (mm^2 / s)	5.3	5.3	2.3 – 6.0

Based on testing the quality of biodiesel contained in the residue remaining showed iodine numbers in the residue average was 55.4. FFA test shows the average value of residual FFA is 0.48%, average acid number of residues is 1.10%, and average density was 8.8690. The results of this analysis showed the residue does not change the quality of the analysis of iodine number, acid number, free-fatty acid levels during the process of separation of tocopherol-rich fraction using molecular distillation.

Results of analysis showed distillate tocopherol concentration is higher than concentrations in the biodiesel. This indicates that the process of separation of tocopherol-rich fraction using molecular distillation can be performed, proved to produce a rich distillate tocopherol.

FFA in distillate test results shows the average value of 0.69%. FFA value is much higher than that contained in the residual FFA as FFA was distillated easier, so that the distillate has a higher FFA concentration. According Martinello (2006), the FFA is more volatile than tocopherol, so the separation of FFA from tocopherol could be done by adjusting the residence time distillation process by regulating the flow rate of material. According to Posada (2007), FFA is distillated almost in every treatment is done, because the FFA concentration is relatively high so that it will be found in the distillate and in the residue.

Conclusion

Separation of the tocopherol-rich fraction of palm oil biodiesel can be made using molecular distillation apparatus. Tocopherol separation process condition of CPO biodiesel using molecular distillation with a flow rate of 1.3 liter/jam-1, 7 liters / hour, distillation temperature 175 ˚ C - 220 ˚ C and 200 rpm rotational speed wipers - 400 rpm successfully separated fraction tocopherol from palm oil biodiesel rich. The results showed tocopherol successful separation is separated as much as 22.9 mg - 605 mg of a total of 1302 mg tocopherol contained in any treatment (2 liters of biodiesel CPO). Tocopherol recovery showed around 35%.

Biodiesel does not indicate quality changes before and after the molecular distillation process. This is supported by the results of analysis of iodine number, free fatty acid levels, acid number, density and kinematic viscosity respectively before and after the molecular distillation process shows a range that is in Indonesian biodiesel standard.

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