Purification of Methyl Ricinoleate on Producing of Cetane Improver

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Abstract. Purification of methyl ricinoleate on a mixture of methyl ester that was derived from castor oil has been conducted. Methyl ricinoleate with high purity is required in the manufacture of additives for improving the cetane number of diesel oil. Purification of methyl ricinoleate was performed by fractional distillation under reduced pressure at 4.5 mmHg. In order to produce of cetane improver, methyl ricinoleate was nitrated with a mixture of HNO_3 and acetic anhydride at 11-13°C for 4 hours. Based on the analysis using gas chromatography (GC) was known that purity of methyl ricinoleate can be increased from 87.2% to 99.5%, with a yield of 30.6% (v/v). FTIR analysis showedthe absorption spectrum at 3440 (1 /cm), which is derived from the vibrations of the -OH (hydroxyl) on the ricinoleate methyl molecules. The results of characterization showed an increase in density of 0.9161 (mg/L) to 0.9171 (mg /L) and the refractive index of 1.4619 to 1.4627. FTIR spectra of nitrated methyl ricinoleateshowedan absorption spectrum at 1627 (1/cm), in which indicates a new compound with nitrate group ($-NO_3$).

1. Introduction

One important parameter for determining the fuel quality is a cetane number. Cetane number is a measure of the combustion quality of diesel oil in a machine [1, 2]. Low-quality of diesel oil is indicated by low the cetane number. Malaysian's diesel hasa cetane number of 50, Thailand of 50, and Singapore of 51[3-4]. Diesel oil with a high cetane number will have a positive impact on engine performance and exhaust emissions[5-7]. Therefore, Indonesian's diesel oil still require the addition of additives in order to get better quality.

Type of additives (cetane improver) that is widely used today is a class of organic nitrate compounds, namely 2-ethyl-hexyl-nitrate (EHN). EHN compound is a derivative of petroleum (nonrenewable). Therefore, some researchers [8-11] tried to find another additive as an alternative. The researchers used triglycerides or fatty acid as a raw material. Firstly, triglyceride was converted into esters, then nitrated into nitrate esters. In acquiring this nitrate ester compound, Porier et al. [8] and Kalam[4]wereinitiallyhydration of the double bond ofcarbon atoms (C=C),then followed by areductionin order to obtain the –OH group (hydroxyl). The –OH group was then nitrated using HNO_3 in order to get mononitrate compound. If -OH group is not ready, nitration will be occurred on C=C bonds and produced thepolynitrate compound.The polynitrate compoundhas high polarity, so solubility in diesel oil is low and emissions of NO_x from the exhaust gas become high[10, 11].

In order to get mononitrate compound, Rabello et al.[11] choose a shorter way by using castor (*Ricinus communis*) oil as raw material. Castor oil was chosen because of the fact that the oil hasricinoleate acid that contains ahydroxyl group (-OH).Ricinoleateacid is the largest component(87-88%)incastor oil. According to Munack[12], there are any otherfatty acids in castor oil, such as palmitate (1-2%), oleate (3-4%), linoleate(5-6%), and stearate (1-2%).In order to produce mononitrate compound as afuel additive, Rabello et al. [11]conducted transesterification of castor oil, then be followed by nitration of methyl ester.

The high diversity of acid in a mixture of castor oil leadhigh types of nitrationproduct.There are many types of ester that derived from the acids tend to increase thepolarity of additive molecules.Beside of hydroxyl group (-OH), C=C is aninteresting site for electrophiles. Therefore, purifying of methyl ricinoleate before being used on nitration processis important.Purification of methyl ricinoleate can be carried out by fractional distillation. Distillation can be conducted because of the differences in boiling point of thecomponent.

2. Methods

2.1. Materials

The materials used werecastor oil (Brataco Chemical Ltd.), methanol (Merck), Na (Merck), HNO_3 65% (Merck), HCl (Merck), acetic acid anhydride(Merck),diethyl ether (Merck), Na_2SO_4 (Merck), universal pH paper (Merck), andaquadest (Chemistry PhysicsLaboratory ofUGM).

2.2. Equipment

Some of the main equipment used are three-necksdistillation flask (Pyrex), reflux condenser (Pyrex), magnetic stirrer (Stuart SB 163),thermometer, magnetic stirring bar, separation funnel (Pyrex), viscosimeter, pycnometer, gas chromatography (GC HewlettPackard 5890 series II, FID, HP5 30 m, column temperature of $300^{o}C$, injection temperature of $150^{o}C$, carrier gas: He, burner gas: $H_2 + O_2$), GC-MS (Shimadzu GC 17A-QP 5000, Impact Electron, Rtx-5MS (5% diphenyl, 95% dimethyl polysiloxane) 30 m, d: 0,25 mm, maximum temperature: 350 ^{o}C, Injector mode: split 1:60, detector temperature: 300 ^{o}C) andFTIR spectrophotometer (Shimadzu Prestige 21).

2.3. Procedure

2.3.1. Transesterification of castor oil.

Two hundred millilitres of methanol and 0.2 g of sodium metal (Na) were added successively into three-necks distillation flask (500 mL). The solution was stirred slowly (100 rpm) for 5 minutes, then 100 mL of castor oil was added into the flask. After all of thecastor oil was added, the stirring speed was increased to 600 rpm and stirred for 24 hours.After the reaction runs for 24 hours, stirring was stopped and the mixture was added into separation funnel (1L). Then, into a separating funnel was added 600 mL of HCl that contains 2 mL of HCl 6 M. The mixture was allowed to stand for ±20 hoursso that form two layers. The upper layer was washed with aquadest until neutral, dried over Na_2SO_4, and filtered. The filtrate (diethyl ether) was then evaporated. The product of transesterification was characterised by determination of density, refractive index and viscosity. Analysisof product was also conducted with GC-MS and FTIR.

2.3.2. Purification by fractional distillation.

Purification of methyl ricinoleate was conducted by fractional distillation using reduced pressure distillation at 4.5 cmHg and the distillate was collected in the three-necks flask (3 fractions). Distillation in this work used 1300 mL of methyl ester. Distillate of each fraction was analysed by gas chromatography (GC), FTIR and measured by volume, density and refractive index.

2.3.3. Nitration of methyl ricinoleate.

Nitration was conducted at low temperature (11-13 °C), using a mixture of ice and water in awater bath. Firstly, 0,3 mL HNO_3 was added in athree-necks flask, followed by 1.5 mL acetic acid anhydride. Furthermore, amagnetic stirrer was operated slowly (200 rpm), while waiting for the temperature in the flask constant. After a constant temperature was reached, then into the flask was added 2.3 mL methyl ricinoleate quickly. Nitration was conducted for 4 hours, then the reaction was stopped by pouring the mixture into a separation funnel, in which already contains 20 mL diethyl ether and 200 mL of cold water. The upper layer (diethyl ether) was washed with aquadest until neutral, then was dried by theaddition of Na_2SO_4 anhydrous. Diethyl ether was evaporated by heating at 80 °C for 30 minutes. The product then analysed by GC and FTIR.

3. Results and Discussion

Transesterification of castor oil produces a mixture of methyl ester compounds. Characterization of methylesterscovers density, refractive index and viscosity. Table 1 showsthe data of physical properties of castor oil before andafter transesterification. The data of density, refractive index, and viscosity of castor oil become lowerafter transesterification. This circumstance was theimpact of reducing on interaction force in the molecules.Originally, fatty acids bonded in glycerol of triglyceride molecule. However, after triglyceride molecules change to esters, one molecule of triglyceride turns into three ester molecules. The interaction between methyl ester molecules will not as strong as on fatty acid.The lower interaction on methyl ester molecule makesthe density of the ester become lower too. The lower of density will impact on reducing of refractive index properties. Transesterification process makesthe molecular size of triglycerides become smaller. The molecular size of triglyceride is about three times of methyl ester molecules. Decreasing on viscosity is as theimpact of decreasing in molecule size.

Table 1. Data of physical properties of castor oil before andafter transesterification

	Density (g/mL)	Refractive Index (n)	Viscosity (cPs)
Before	0.9537	1.4785	297.4
After	0.9161	1.4619	19.8

Chromatogram of transesterification product was presented in Figure 1. Transesterification of castor oil produced a mixture that consists five kinds of methyl esters compound. Based on the analysis using mass spectroscopy (mass spectra are not presented in this article), it was known that these compounds are methyl palmitate (0.8%), methyl linoleate (3.2%), methyl oleate (6.8%), methyl stearate (1.9%) and methyl ricinoleate (87.2%).
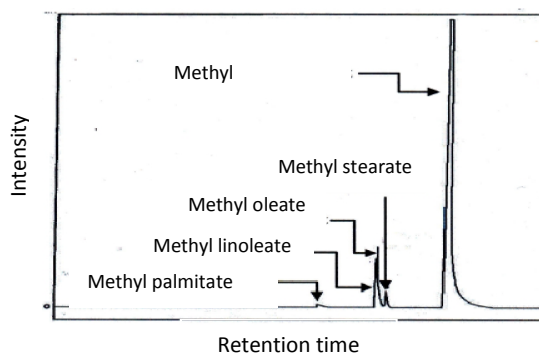

Figure 1.Chromatogramof methyl esters from castor oil.

Based on GC data showed that methyl ricinoleate still mixed with another methyl ester, where the content of methyl ricinoleate still relatively low in order to produce the additive. This circumstance is necessary to beincreasedby fractional distillation. On the process of fractional distillation was observed temperature data for every 2 minutes. This data can be used in predictionwhen distillate of methyl ricinoleate with high purity already commenced.Figure 2shows(area Fraction I and II) a rapid of temperature change for each observation time, so that the graph like resembles a staircase. Such circumstances indicate that the purity of methyl ricinoleate in the area is still low. It has been proved by the data of chromatogram as shown in Figure 3 (FI and FII).

Figure2 shows that in the 46th to 58th minutes, the distillation temperature finished at 186 °C. Starting with next minute (60th), distillation takes place at a temperature of 188°C for a long time up to the 345th minutes (for 275 minutes). Figure 2shows clearly that initial distillate in fraction III is not yet optimal. Therefore, the third fraction of distillatewas separated into IIIa and IIIb. Fraction IIIa was stopped at 110th minutes, and collection of distillate was continued for fraction IIIb. After all distillate of fraction III was run out, distillation temperature decreased. This suggests that the distillation finished.
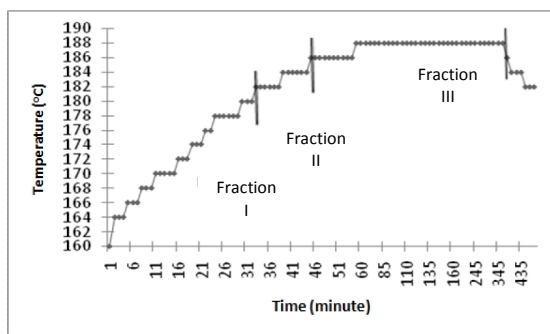

Figure 2. Graph of distillation temperature versus time

Table 2 shows thevolume of distillation, where total for Fraction III (FIIIa + FIIIb) was 761 mL or by 58 % of its initial volume (1300 mL). The density and refractive index for FIIIa and FIIIb seem larger than thevalue in FI and FII. Increasing of density will be accompanied by increasing on refractive index, in which consistent with the data of density and refractive index. The purity of methyl ricinoleate increase from FI to FIIIb. Methyl ricinoleate has a boiling point of 412 °C at 760 mmHg (1 atm), while the other has a much lower boiling point. Methyl stearate = 295 °C, methyl palmitate = 338 °C, methyl oleate = 352 °C, and methyl linoleate = 349 °C [13]. Methyl linoleate has a boiling point equal to the boiling point of methyl linoleate [14]. Thus, by fractional distillation under reduced pressure method, purification of methyl ricinoleate can be conducted easily.

Table 2. Physical data properties of methyl ricinoleate fractionation results inpressure reduction

Fraction	Volume (mL)	Density (g/mL)	Refractive Index (n)	Purity (%; GC)
FI	149	0.8952	1.4578	38.82
FII	211	0.9107	1.4611	70.06
FIIIa	363	0.9168	1.4622	97.86
FIIIb	398	0.9171	1.4627	99.52

According to Yao et al. [14], purity of methyl ricinoleate can be increased by extraction using hexane, then washed with a solvent. The solvent is a mixture of methanol, water and acetic acid (90:10:1). The result of purification showed that purity of methyl ricinoleate was originally 88% can be improved to more than 98.5% with a yield of 53 % (w/w). Although this method produced high purity of methyl ricinoleate, it needs many steps in the process.

The castor oil methyl ester from purification with the highest purity (FIIIb) was then analysed by FTIR spectrophotometer. Figure 4a shows there issome absorption spectrum of the methyl ester of castor oil. The main absorption spectrum of functional groups present at 3440, 1743 and 1658 (1/cm).The spectrum of absorption at 3440 (1/cm) is derived from the vibration of O-H (hydroxyl group). The hydroxyl group in the ester compound resulted from methyl ricinoleatemolecule.Absorption spectrum at 1743 (1/cm) is derived from the range of C=O contained in all the methyl ester, whereas the spectrum in 1658 (1/cm) is derived from the range of C=C of the methyl ester of castor oil (except methyl palmitate and methyl stearate). Other absorption spectra provide additional information aboutester compound of the result of esterification.

Castor oil methyl ester from FIIIb then was analysed by FTIR spectrophotometer. Figure 3a shows some absorption spectrum of methyl ester castor oil. The main absorption spectrum of functional groups present at 3440, 1743 and 1658 (1/cm). The spectrum absorption at 3440 (1/cm) is derived from the vibration of O-H (hydroxyl group). The hydroxyl group in the ester compound resulted from methyl ricinoleate molecule. Absorption spectrum at 1743 (1/cm) is derived from the range of C=O contained in all methyl ester, whereas spectrum at 1658 (1/cm) is derived from C=C of the methyl ester of castor oil (except methyl palmitate and methyl stearate).
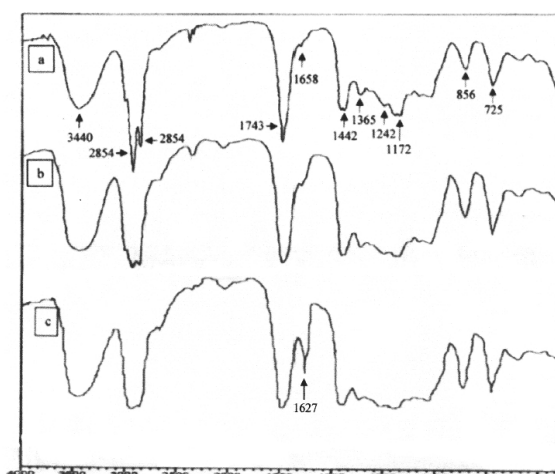

Figure 3. a) FTIR spectra of methyl ricinoleate before purification), b) FTIR spectra of methyl ricinoleate after, c) FTIR spectra of nitrated methyl ricinoleate at low temperature (11-13 °C) for 4 hours

Figure 3.b is FTIR spectra of purified methyl ricinoleate.Spectrain Fig 3b shows an increment of theareaat 3440 (1/cm). This increment is estimated to have acorrelation with thelevel of methyl ricinoleate purity. Figure 3c is FTIR spectra of nitrated methyl ricinoleate. Figure 3c shows a new spectrum at 1627 (1/cm), as a result from N-O stretching vibration of nitrate group($-NO_3$). Nitration on methyl ricinoleate with high purity used a mixture of HNO_3 and acetic anhydride. This mixture will produce acetyl nitrate that acts as a carrier of nitronium ion. Mechanism of   nitronium ionforming had been shown in the formerly literature [10]. Nitration on methyl ricinoleate will take place at the –OH group [15], then producemethyl ricinoleate nitrate.However, nitration can also occur at the C=C of methyl ricinoleate molecule. Nitration at C=C of methyl ricinoleate molecules can be minimised by conducting the nitration at low temperatures and a limited amount of HNO_3 [10].

4. Conclusion

Purification of methyl ricinoleatefrom oil methyl ester mixture can be conducted by fractional distillation under reduced pressure at 4.5 mmHg. Methyl ricinoleate purity can be increased from 87.2% to 99.5%. The distillatefrom fractional distillation of methyl ricinoleate was collected at 186-188°C.Nitration

of methyl ricinoleate at temperatures of 11-13°C for 4 hours using a mixture of HNO$_3$ and acetic anhydride has produced nitrate group compounds of methyl ricinoleate

Acknowledgements

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