THE EFFECT OF INITIATOR COMPOSITION, TEMPERATURE, AND TIME ON ESTER POLYMERISATION PROCESS OF PALM FATTY ACID DISTILLATE

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ABSTRACT

Palm Fatty Acid Distillate (PFAD) as a byproduct of the processed of palm oil has great potential to be used as raw material for polyester synthesis. The purpose of this research is to study ester polymerisation from PFAD with the composition of initiator, time and temperature as the parameters. First, the esterification process was done by the reaction of PFAD and methanol that used sulfuric acid as catalyst. The reactant composition was 1:8 molar ratio, speed of stirrer at 150 rpm, and H_2SO_4 composition is 1% (w/w) PFAD with temperature at 70° C for 2 hours. The polymerisation process was done by the reaction of esterification stage product and mixed with benzoyl peroxide as initiator. The variation for this stage were the composition of benzoyl peroxide 1%, 5%,and 9% (w/w) of methyl ester, polymerisation time 4, 5 and 6 hours and polymerisation temperatures of 140, 150 and 160° C. The result showed that the esterification stage product was obtained methyl ester and GC-MS analysis showed that the purity of methyl esters is 90,1%. Polymerisation product that is obtained a polyester but still have vinyl group in the component of the product. Based on the results of polymerisation reaction of the end product, dark and thick and has a viscosity of 180-200 cp. Based on the test results of GC-MS the composition of the methyl ester was reduced from 27.67% to 5.62% as the product of polymerization process which mean that the methyl ester have been converted. The R^2 in this study gained 0.9663 which means a significant and lack of fit value of 0.1341 which means insignificant then the variable had a p-value of 0,0002 for the model which it less than $\alpha = 0.05$ with variables that had a significant impact on model.

Key words: benzoyl peroxide, palm fatty acid distillate, polyester, synthesis

1. INTRODUCTION

Palm oil production in Indonesia, especially in Riau has increased every year. Palm plantation area reached 1,673,771 ha in 2008 and increased 2,372,402 ha in 2012. The increased of plantation area led to the increasing of oil production of 5,764,201 tons of fresh fruit bunches (FFB) in 2008 to 7,340,809 tonnes of FFB in 2012 (BPS Indonesia, 2012). The increasing oil production, opportunities for increased use of oil and its derivatives are also made parties to increase the effectiveness and economic value for our country. CPO as raw material for oleochemical-based downstream industries begins with the CPO purification process in order to obtain Refined bleached deodorised Palm Oil (RBDPO).

The purification process consists of several stages, namely pospatida removal, unwanted color removal and deodorizing. Deodorizing process step are performed in physic way, steam stripping. At this stage Palm Fatty Acid Distillate (PFAD) will separate as 6% of CPO feed (Yelmida et al, 2012).

One derivative of palm oil processing is PFAD. With the increase in palm oil production suggests that the acquisition PFAD increasing. Although PFAD is a

byproduct, but it still has potential to be used without disturbing the availability of food, so that the use of palm oil byproducts process more extensive. PFAD as a byproduct has a huge potential to be used as raw material for polyester products (Tanjung et al, 2013).

2. MATERIALS AND METHODS

Materials used in this research is Palm Fatty Acid Distillate (PFAD) from PT. Wilmar Bio-energy, methanol, sulfuric acid MERCK™ 1% (w / w) PFAD for esterification process, benzoyl peroxide MERCK™ 0.1% (w / w) methyl ester as initiator of the polymerization reaction, ethylene glycol MERCK™ as polymerization reactants.

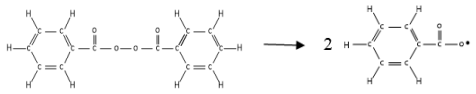
First, the esterification reaction is started by reacting PFAD which already being tested using GC-MS and methanol with the addition of sulfuric acid catalyst in the reactor is equipped with a reflux condenser and a stirrer inversely with the temperature 70 ° C. The molar ratio PFAD and methanol is fixed variables 1: 8 with a catalyst 1% by weight sulfuric acid ALSD. The product is expected as FAME (Fatty Acids Methyl Esters).

Furthermore, the polymerization process by reacting FAME with benzoyl peroxide as initiator in the reactor with the variation of initiator composition of 1%, 5% and 9% by the weight of FAME then temperature of 140, 150 and 160^{o} C and the time variation of 4, 5 and 6 hours. After the polymerization reaction, ethylene glycol being added in the ratio 1: 1 into the reactor at a temperature 175-200^{o} C and reaction time of 6 hours.

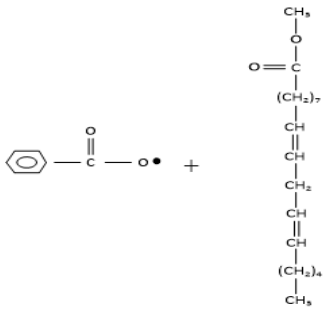
To determine the polymerization reaction has occurred, the test was analyzed using FTIR (Fourier Transform Infrared) to characterize the molecular structure of the functional groups and GC-MS (Gas Chromatography and Mass Spectrometry) to determine its composition also the physical properties of the polyester formed should be calculated on the viscosity for each sample.

The reaction that be used in the polyester synthesis in this study is free radical polymerization reaction which consists of three stages of reaction, there the initiation stage, the propagation stage and termination phases.

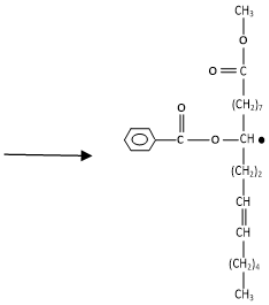
Initiation Phase



Free Radical

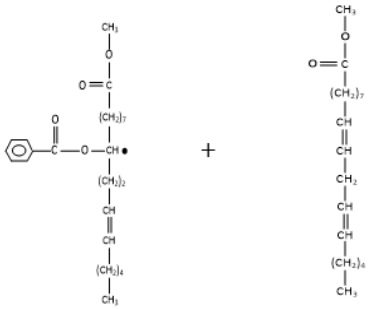


(Free Radical) (*Octadecadienoic Acid, Methyl Ester*)

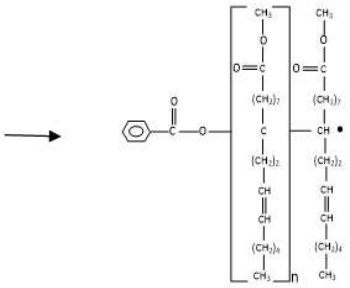


Methyl ester (Radical)

Propagation Phase

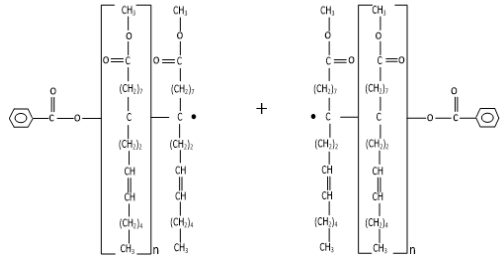


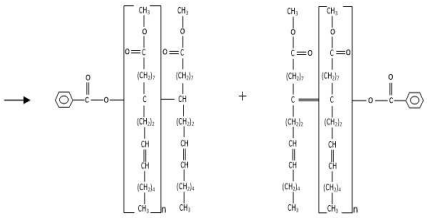
Methyl ester (Radical) - *Octadecadienoic Acid, Methyl Ester*)



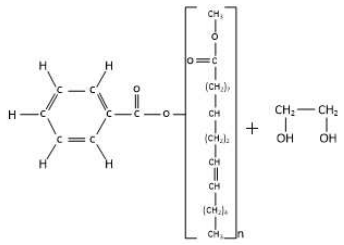
(Doubled Methyl Ester with radical)

Termination Phase

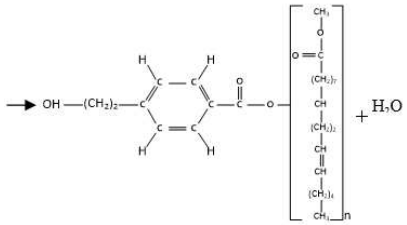




(Methyl Ester Dimer (Methyl Ester Dimer)



(Methyl Ester (Trimer) (Ethylene Glycol)



Polyester

Polyester resins typically used in any applications that use high temperatures, such as in electrical applications and corrosion resistance. In addition, the polyester resin is also needed in applications that have a chemical resistance for decades. Polyesters are polar, so the more polar conditions will decrease the corrosion attack of components made from unsaturated polyester (Bramantyo, 2008).

The purpose of this research was to study the polymerization esters from Palm Fatty Acid Distillate (PFAD) using benzoyl peroxide as initiator.

3. RESULT AND DISCUSSION

3.1 Result Analysis Esterification Reaction

Esterification reaction occurs between PFAD) and methanol with mole ratio of 1: 8 using sulfuric acid as catalyst of 1% (w / w) ALSD. This reaction lasted for two hours at a temperature of 70 ° C. To determine the composition and purity of the methyl ester produced test used GC-MS (Gas Chromatography and Mass Spectrometry). The results of GC-MS testing methyl ester can be seen in Table 1. Table 1 shows that the total purity of the methyl ester of the overall composition that is equal to 88.42% and the rest is a fatty acid component which has not participated reacted into esters.

Table 1. Wave Number of Methyl Ester

Sample	Wave Number (cm^{-1})	Groups	Compound
FAME before Polymerize	3336,03 – 3308,06	O-H	Carboxylate Acid
	1717,68	C=O	ester
	2924,21 – 2833,55	C-H	Alkenes
	719,48 – 602,78	CH_2	deformation
	2026,92 - 1990,27	X=C=Y	Isocyanate, isothiocyanate
	1742,76	C=O	ester
	1464,03 – 1418,71	CH2-C=O	CH_2 deformation
	1362,77 – 1116,83 1025,21	C-X, C-O	Floride,bromide,chloride

Tanjung and Manurung et al (2013) found the methyl ester purity is 82.23%. To prove the formation of methyl esters also tests other analysis is the analysis of FT-IR (Fourier Transform Infrared). The test results of FT-IR of the methyl ester can be seen in Figure 2.

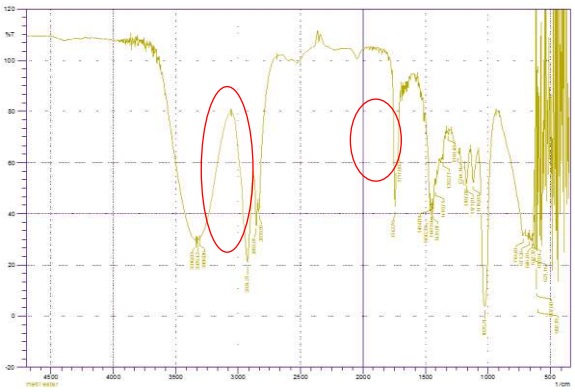


Figure 2. FTIR (*Fourier Transform Infrared*) Result for Methyl Ester

Based on Figure 2 can be seen at wavelengths of 1742.76 cm-1 indicating the ester group (C = O) in the range of 1730-1750 cm^{-1} (Pavia et al, 2009). In addition, there are at wavelengths of 1024.25, 1115.87, 1171.81, 1197.85 and 1244.14 cm^{-1} included in the range of 1000 to 1300 cm-1 shows the acid group (C = O) (Pavia et al, 2009).

Table 2. GC-MS Result for Methyl ester

Methyl ester compisition	Acid Type	% area
Dodecanoic Acid	Lauric Acid (saturated)	8,56
Tetradecanoic Acid, Methyl Ester	Miristic Acid (saturated)	1,61
Tetradecanoic Acid	Miristic Acid (saturated)	1,35
Hexadecanoic Acid, Methyl Ester	Palmitic Acid (saturated)	51,09
7 - Octadecanone	Oleic Acid (unsaturated)	1,68
9,12 – Octadecadienoic Acid, Methyl Ester	Linoleic Acid (unsaturated)	5,06
11 – Octadecenoic Acid, Methyl Ester	Oleic Acid (unsaturated)	27,67
Octadecanoic Acid, Methyl Ester	Linoleic Acid (unsaturated)	2,99
		100

Viscosity test results of the methyl ester obtained in the amount of 0.00374 poise. Data purity of the methyl ester is very much needed in the calculation of the composition of benzoyl peroxide in the polymerization stage. In a test of GC-MS product of the esterification reaction, there are no more methanol content so it can be assumed to methanol has been completely reacted or partially evaporated.

3.2 Analysis of Polymerization Reaction

Methyl ester which has formed proceed to the stage of polymerization with the assistance of benzoyl peroxide as initiator as 0.1% (w/w) of methyl ester. Benzoyl peroxide is inserted in solid phase (powder). Benzoyl peroxide which used has a melting point at a temperature of 102-105^{o} C. The polymerization reactions will be carried out at a temperature 140-160^{o} C so as benzoyl peroxide had melted at the temperature of the polymerization reaction.

Methyl ester monomer which is to be initiated by benzoyl peroxide on a double bond which is possesed monomer that makes the bonding between monomers to form dimers, trimers, untill polymer. The polymerization reactions using benzoyl peroxide initiators included in radical addition polymerization reaction which has three stages: initiation, propagation and termination (Fried, 2003).

Based on Manurung et al (2013), the addition of ethylene glycol in the polymerization reaction is the effort to minimize the water content. Moreover, the addition of ethylene glycol also serves as lengthening of the polymer chain (Budi et al, 2009). By increasing the length of the polymer chain will increase the molecular weight of the polymerization reaction product, resulting in a change in the molecular weight of the reactants into the final product.

Table 3. Numbers Wave Methyl Ester After Polymerization Reaction

Sample	Wave Number (cm^{-1})	Gugus Fungsi	Tipe Senyawa
Methyl Ester After Polymerize	3303,8	O-H	Asam Karboksilat
	2854,07 dan 2923,53	C-H	Alkena
	882,36 – 862,11 721,20		
	2026,92 - 1990,27	X=C=Y	Isosianat, isotiosianat
	1741,91	C=O	ester
	1456,82 dan 1435,78	CH_2-CH=O	CH_2 deformasi
	1367,12 – 1171,48	C-X, C-O	Florida, klorida, bromide, iodida
	1084,73 – 1036,20		

The end product of the polymerization reaction which has been analyzed using FT-IR test to determine the group of ester (C=O) which is an active group of the monomer. Figure 3 is the FT-IR test results from the test samples. Based on Figure 3 are at a wavelength of 1738.90 cm^{-1} indicating the ester group (C = O) in the range of 1730-1750 cm^{-1} (Pavia et al, 2009).

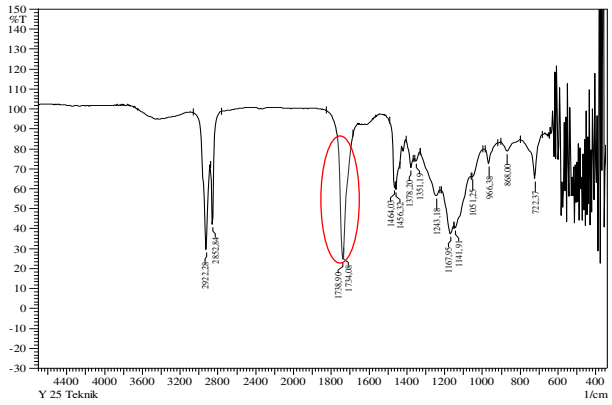


Figure 3. FT-IR Test Result for Sample made by variation T = 160 ^oC, t = 6 Jam, and $C_{initiator}$ = 1%

Besides test FT-IR has done for the final product at the polymerization stage with variable temperature 160 ° C and a polymerization time of 6 hours also tested GC-MS to determine the composition of the ester remaining after the polymerization reaction is done.

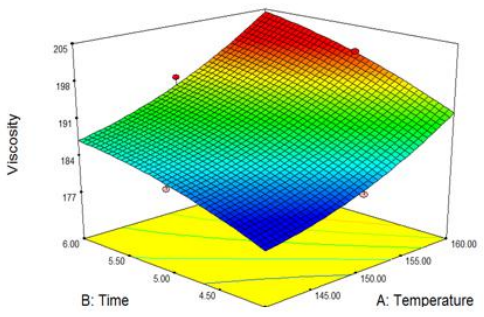
Chromatogram esterification reaction results indicate that the compound Octadecanoic acid methyl ester is the second largest component of an area of 27.67%. While chromatogram for sample results show that the polymerization reaction is the largest compound Octadecanoic acid, (2-pheny-1,3-dioxolan-4-yl) methyl ester ($C_{28}H_{46}O_4$) 5.62%. Decreasing the percentage of ester showed that the ester compound has been converted through polymerization.

3.3 Effect of Temperature and Time initiator composition on Polymerization Reaction

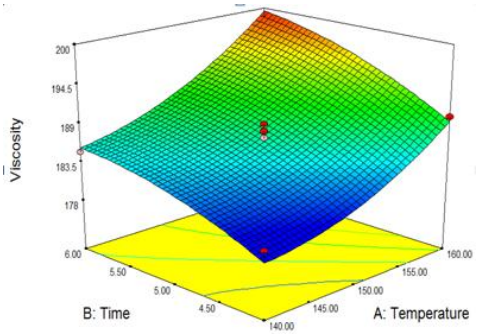
In this study, we have time, temperature and initiator composition in the polymerization reaction becomes variable changes. Based on viscosity test results we have obtained the optimum temperature and time conditions. The increase in viscosity occurs from a temperature of 140 ° C to 160 ° C temperatures. And the optimum initiator composition is the lowest amount which have the highest viscosity for all sample.

The increasing polymerization reaction time caused by the higher temperatures so that its density was not able incompressible (incompressible) and did not cause significant changes in density (Handy et al, 2013).

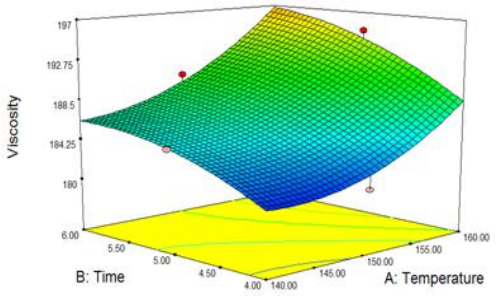
The Effect of time on the results of a viscosity test is the longer of time for the polymerization reaction, the viscosity increased. The effect of time and temperature on the viscosity of the polymerization reaction can be seen in Figure 4.



a.



b.



c.

Figure 4. Relations of Temperature and Time Reaction with Viscosity Initiator composition of a. $x_3 = 1\%$; b. $x_3 = 5\%$; dan c. $x_3 = 9\%$. by weight FAME

The relation of the variable with response can be significant because in the theory it always make differences for each variable to read by the response.

Based on the Tanjung and Manurung et al (2013) have a relation to the polymerization reaction time with viscosity values which is, the longer of the reaction time, the viscosity value is increasing as well. This research have the same result on the relation of time with viscosity and also it assisted by the temperature increases for any difference value of viscosity.

4. CONCLUSION

The result showed that the esterification stage product was obtained methyl ester with density 0,9809 g/ml, viscosity 185 cp and GC-MS analysis showed that the purity of methyl esters is 88,9%. Based on the results obtained by the polymerization reaction of the end product, dark and thick and has a viscosity of 177-205 cp.

Based on the FT-IR test results for overall sample after the polymerization reaction, an absorption band is still a vinyl group (-CH = CH2), which indicates there is still a bond that has not been cut. Based on the test results of GC-MS samples obtained after the polymerization reaction, the composition of the methyl ester was reduced from 27.67% to 5.62%.

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