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Effect of Concentration of Catalyst (BF_3-Diethyl Etherate) on Synthesis of Polyester from Palm Fatty Acid Distillate (PFAD)

Renita Manurung[1], Ahmad Rozi Tanjung[2], Ida Ayuningrum[3]

Department of Chemical Engineering, University of Sumatera Utara

Jl. Almamater Komplek USU Medan 20155 Indonesia

Email : [2]rozi.tanjung@y7mail.com

Abstract - Palm Fatty Acid Distillate (PFAD) can be used as raw material for synthesis polyester. The aim of this research is to synthesis of polyester and to determine the effect of concentration of catalyst on polymerization methyl ester PFAD. The esterification stage was done at temperature 70°C, reaction time 120 minute, reactant ratio 1:8 (PFAD: methanol), concentration of catalyst (H_2SO_4) 1% (w/w) PFAD; polymerization stage was done at temperature 126-132°C, polymerization reaction time 4 hours; variation of concentration of catalyst (BF_3-diethyl etherate) 0%, 6.9%, 9.2%, 11.5% (w/w) methyl ester; and polyesterification stage was done at temperature 175-200 °C, reactant ratios (w/w) 1:1 (polymerized ME : ethylene glycol), reaction time 4 hours and all of stage was stirred at 150 rpm. The results showed, in the esterification stage was obtained methyl ester with iodine value 77.29 g I_2/100 g, viscosity 6.90 cP, density 859.91 kg/m^3 and analysis by using GC-MS showed that the purity of methyl ester was 82.23% and molecular weight 267.97 g/mol. Decreasing in iodine value from 77.29 I_2 g/100 g to 74.97-59.99 g I_2/100 g indicated that the polymerization process had taken place. In polyesterification stage was obtained light brown colored liquid for concentration of catalyst 0%; viscous, light brown colored liquid for concentration of catalyst 6.9%; and gel polyester, viscous, dark brown colored solid at room temperature for concentration of catalyst 9.2% and 11.5% with acid value from 8.19 to 26.14 mg KOH/g, viscosity from 0.07 to 15.2 P, and molecular weight 288.81 to 1522.07 g/mol which is more suitable for applications of modified polyester. Analysis by using GC showed that the purity of polyester is equal to 65.49%.

Keywords— *polyester, palm fatty acid distillate, polymerization concentration of catalyst, biodegradable polymer*

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I. INTRODUCTION

Indonesia is one of the largest palm oil producer in the world [1]. In the processing of palm oil is obtained some derivatives such as Palm Fatty Acid Distillate (PFAD) [2]. PFAD has a potential useful as a raw material in the synthesis of polyester. Polyester has many uses such as for making bottles, films, tarpaulin, canoes, liquid crystal displays, holograms, filters, fiber and etc [3]. Polyester has many advantages, resistant to humidity and UV when left in the open air. Polyester fiber have high strength and low water absorption when it is compared with other industrial fibres [4].

Polymer is the most important chemical industrial products that are used in many applications. Almost the most current polymer is produced from petrochemical substance that cannot be renewed. Therefore, the alternative material needs to be known [5]. Currently, vegetable oils are excellent source of renewable materials an alternative material for oil-based polymers because of ecological and economical concern.

Polyesterification is a process of condensation or step-growth polymerization where in the process will be produced polyester and water or alcohol as by product. Direct reaction of diacids or anhydrides with diols are often avoided because of the high temperatures required to completely eliminate water. However, this reaction used to produce low molecular weight. Using dimethyl ester has been used to advantage instead of direct esterification with diacid or dianhydride because reaction is fast and dimethyl ester is often more easily purified and has better solubility characteristics. The polyesterification becomes a much more economically feasible reaction when it is catalyzed by an external acid [6]. In this paper,

polymerization will be catalyzed by boron trifluoride diethyl etherate as strong acid. Catalyst of polymerization has a function to accelerate the reaction by produce an active group toextend the polymer chains [7]. Therefore, it is important to determinethe effect of concentration of catalyston polymerization methyl ester PFAD.

II. Materials and Methods

Main materialsthat are used in this researchsuch as PFAD, BF_3-diethyl etherate, methanol, sulfuric acid and ethylene glycol. The main equipments are a glass batch reactor, a hotplate with magnetic stirrer, reflux condensor and thermometer.

Esterification stage [8], that is reaction between PFAD and methanol was held in a glass batch reactor on the top of a stirring hotplate for 120 minutes with mole ratio 1:8 at 70^{o}C by using 1% sulfuric acid (w/w) and 150 rpm stirring. Density (picnometer), viscosity (viscosimeter Ostwald), iodine value (AOAC 920.158) and composition (GC-MS) of product methyl ester was analyzed. Polymerization stage [9], that is reaction methyl ester by using catalyst BF_3-diethyl etherate with concentration was varied from 0%, 6.9%, 9.2% and 11.5% (w/w) at 126-132^{o}C for 4 hours and 150 rpm stirring. Iodine value of polymerized methyl ester was analyzed.

Polyesterification stage [9], that is reaction between polymerized methyl ester and ethylene glycol in the same reactor for 4 hours with mass ratio 1:1 at 175-200^{o}C, 150 rpm stirring and sampling was performed every 1 hours for analysis of acid value (ASTM D4662-03). Viscosity (viscotester VT-04F), molecular weight (the end group method), structure (FT-IR) and composition (GC) of polyester was analyzed.

III. Results and Discussion

The initial material that was used for the synthesis of polyester was methyl ester by esterification of methanol and PFAD by using sulfuric acid as catalyst. The result of analysis composition PFAD by using GC-MS was shown in Figure 1.

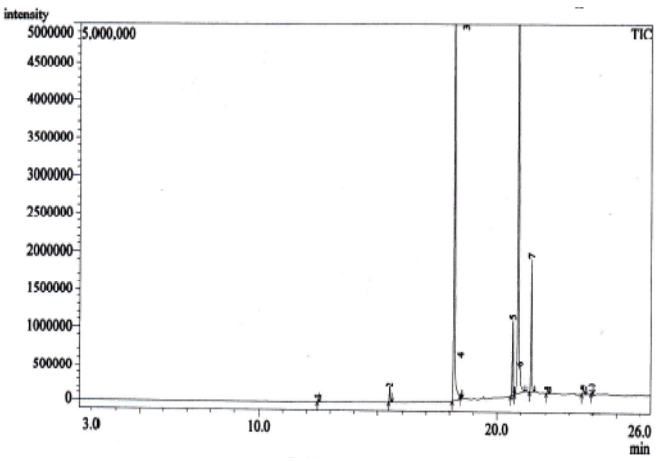
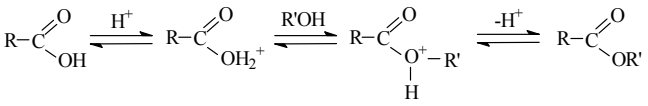


Figure 1. GC-MS Chromatogram of PFAD

GC-MS showed that the average molecular weight of PFAD was 270,84 g/molewith 53,27% unsaturated fatty acids. PFAD would be reacted to produce methyl ester by the following reaction (euation 1):



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The result of analysis composition methyl ester by using GC-MS was shown in Figure 2.

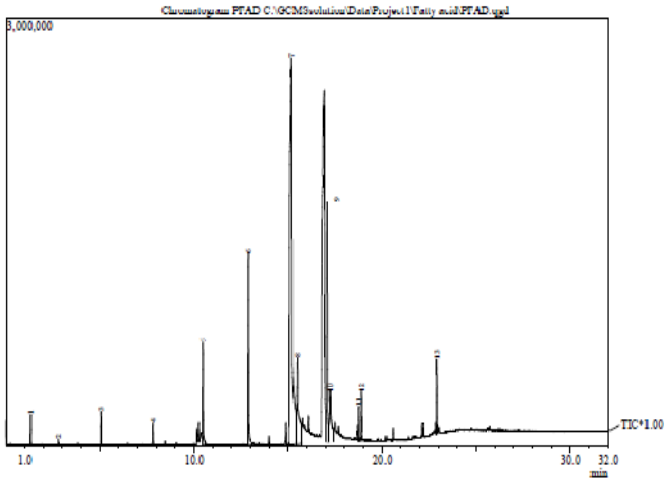


Figure 2. GC-MS Chromatogram of Methyl Ester

GC-MS showed that the average molecular weight of PFAD was 267,97 g/mole with the purity 82,23%. Methyl ester would be used as a raw material for polyester. Analysis of the characteristics of methyl ester PFAD were shown in table 1.

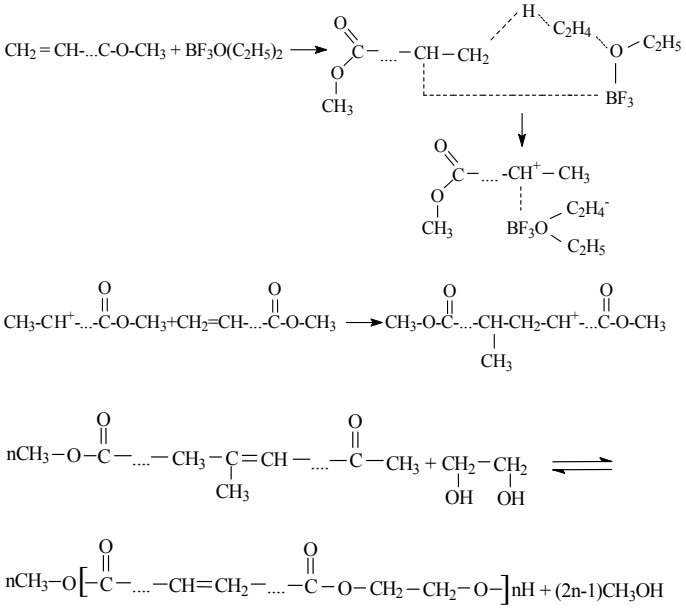
Table 1. Characteristics of Methyl Ester PFAD

Parameter	Value
Iodine Value	77,29 g I_2/100 g
Viscosity (30 ^{o}C)	6,90 cP
Density (30 ^{o}C)	859,91 kg/m^3

Polymerization reaction stage of methyl ester PFAD was performed by using catalyst boron trifluoride diethyl-etherate and then polyesterification stage of polymerized methyl ester and ethylene glycol to produce polyester following the reaction as shown in equation (2). For concentration of catalyst 0% were obtained light brown colored liquid polyester. For concentration of catalyst 6.9% were obtained viscous, light brown colored liquid polyester; and for concentration of catalyst 9.2% and 11.5% were obtained gelpolyester, viscous, dark brown colored solid at room temperature.Polyester that synthezed has a group of molecules that can be identified by using FT-IR. The result of analysis spectrum of polyester was shown in Figure 3.

An ester compound was characterized by the presence of stretching band C=O, C-O and O-H [10]. The formation of polyester was shown by vibration peak at wave number 1751,36 cm^{-1} that indicated a stretching band C=O ester for all run. The difference between the C=O group of acid and ester wasat wave number 1730-1700 cm^{-1} for acid where as at wave number 1760-1793 cm^{-1} for ester [11]. On the other hand, the weakening of the stretching band O-H hydrogen bond at wave number 3500 cm^{-1} - 3400 cm^{-1} supported the formation of polyester. Polymerization was characterized by the

absence of vinyl group (-C = CH_2-) at wave number 990 cm^{-1} - 910 cm^{-1} that indicated decreasing of unsaturated bond. This means that polymerization reactions occur on termination of a double bond. The peak vibration that has formed is the presence of C-H group absorption at wave numbers 732,95 cm^{-1}, 871,82 cm^{-1}, 972,12 cm^{-1}, and 2792,93 cm^{-1}, 2939,52 cm^{-1} and C-H alkyl group at wave numbers 1465,90 cm^{-1}. The result of analysis qualitative for composition polyester by using GC was shown in Figure 4.



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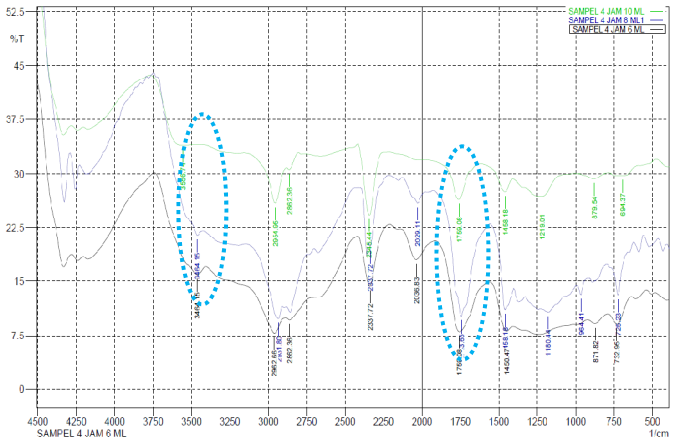

Figure 3. FT-IR Spectrum of Polyester

Analysis of polyester by using GC shown the purity of polyester was 65.49%. Effect of concentration of catalyst on iodine value of polymerized methyl ester was shown in Figure 5. Figure 5 showed that iodine value tends to decrease with increasing in concentration of catalyst. The most important parameter in the synthesis of a polymer was the number of double bonds that exist in a sample which can be shown by iodine value.

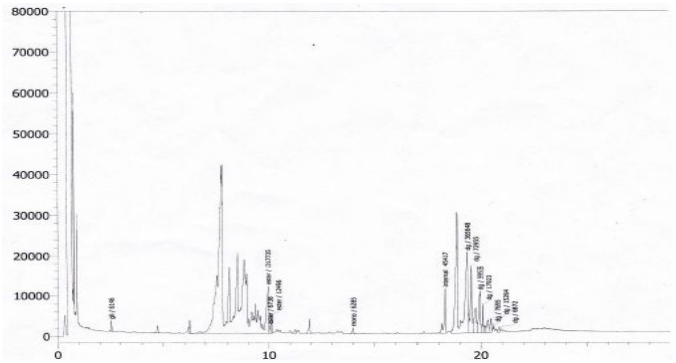

Figure 4. GC Chromatogram of Polyester

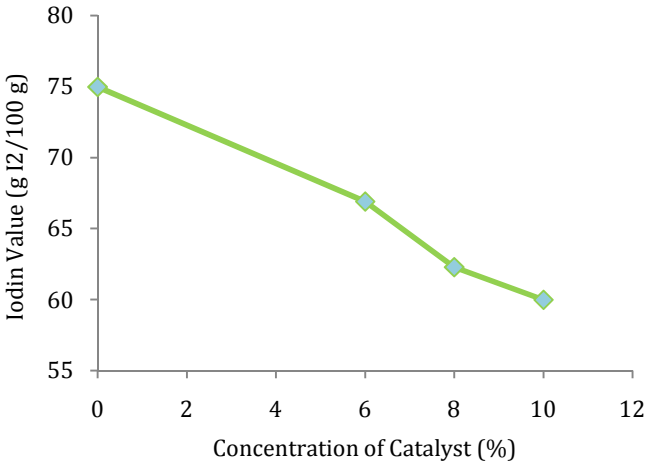

Figure 5. Effect of Concentration of Catalyst on Iodine Value of Polymerized Methyl Ester

With the increasing in concentration of catalyst would decrease iodine value and tend to a constant value [12]. This is suitable with the results that wasobtained in this research. In addition, the reduction in iodine value could be observed visually by the occurrence of a change of color along the process of polymerization. Iodine value will affect the appearance of the oil, the higher iodine value will be clear appearance of such oils [13]. Decreasing in iodine value would influence to be darker color of sample. The result showed that with the increasing in concentration of a catalyst would influence to appearance of product polyester that could be shown in table 2. Effect of polyesterification reaction time on acid value of polyester was shown in Figure 6. Figure 6 showed that acid value decreased with increasing polyesterification reaction time and without adding of a catalyst would not effect on acid value. Analysis of acid value was done to find out the progress of the polyesterification.

Table2. The Characteristic of Polyester

Concentration of Catalyst	Appearance
0 %	light brown colored liquid
6,9%	polyester viscous, light brown colored liquid polyester
9,2 and 11,5%	gelpolyester, viscous, dark brown colored solid at room temperature

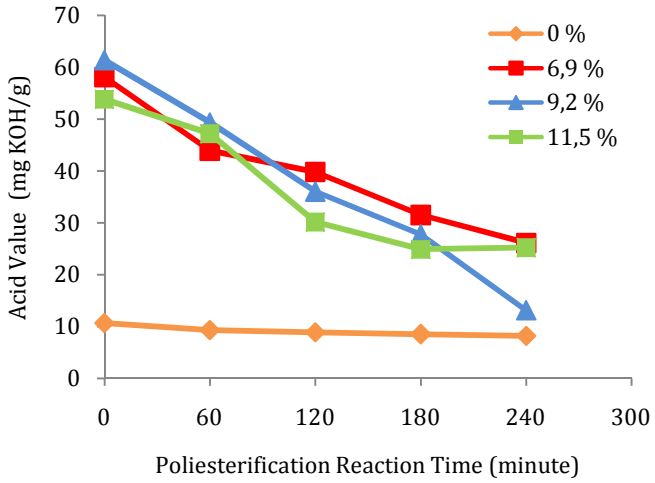

Figure 6. Effect of Polyesterification Reaction Time on Acid Value of Polyester

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The reaction was assumed to take place if acid value decreased. Decreasing in acid value happened because of extension of the chain of reactive carboxyl to form polymers [3]. Acid value could be used as a parameter of quality polyester. The higher acid value indicated quality of polyester would get worse. This is due to the high acid value showed high ability of material to absorb water [3]. Commercial polyester in the market had a standard acid numbers ≤32 mg KOH/g [14]. Polyester that was obtained in this study had acid value ≤32 mg KOH/g, therefore it was polyester with a good quality of acid value. Effect of concentration of catalyst on molecular weight of polyester was shown in Figure 7.

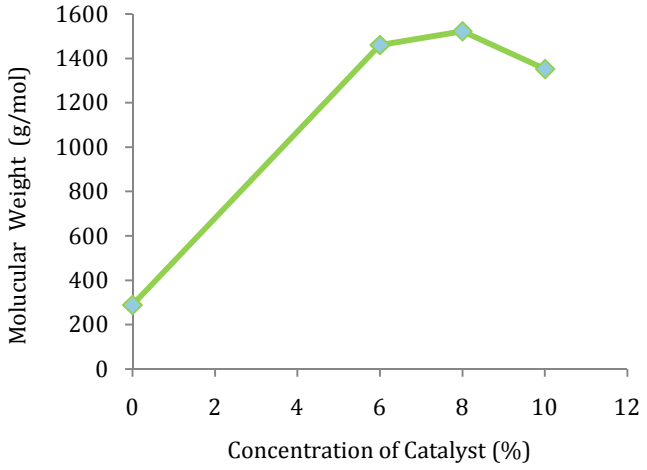

Figure 7. Effect of Concentration of Catalyst on Molecular Weight of Polyester

Figure 7 showed that molecular weight fluctuated with increasing in concentration of catalyst. Increasing in concentration of catalyst would increase active site to eliminate the double bonds that exist on samples [12]. In addition, increasing in concentration of catalyst would increase the mileage (g polymer per mg of catalysts). A greater concentration of catalyst would increase the number of active centre which would initiate the polymerization so that the amount of the resulting polymer was increasing [15].

Molecular weight of polymer was the main attention in practice of synthesis polymer. Polyester had the carboxyl end group and hydroxyl group at the other end [16]. Zhang, et. al. (1994) used end group methods to determine molecular weight in the synthesis of polycaprolacton [17]. Molecular weight of polyester in this research was also determined by end group methods. Polyester with linear high molecular weight polymer, was generally thermoplastic with a molecular weight about 10,000 – 30,000 g/mole. High molecular weight of polyester could be used for the application of powder coating and drying binder. Polyester with low molecular weight that is between 500-7,000 g/mole. Polyester with low molecular weight may be linear or branched with carboxyl and hydroxyl end group. For special purposes, polyester with low molecular weight 1,000-5,000 g/molewas modified due to functional group being more reactive than polyester with high molecular weight [18]. Polyesterification was reversible polycondensation reaction [3]. The results showed that increasing in concentration of catalyst would increase molecular weight. But at concentration of catalyst 11.5%, decreasing in molecular weight had occured. This condition happened because of increasing in concentration of polymer that had formed caused equilibrium conditions had turning to form reactants back.

The results showed thatproduct of polyester had a range of 1,352.26 – 1,522.07 g/mole. Therefore, this polyester could be counted polyester with relatively low molecular weight that was more suitable for the application of the modified polyester. The low molecular weight polyester was formed due to the raw material which was used was a methyl ester of PFAD which had alittle double bonds. Effect of concentration of catalyst on viscosity of polyester was shown in Figure 8.

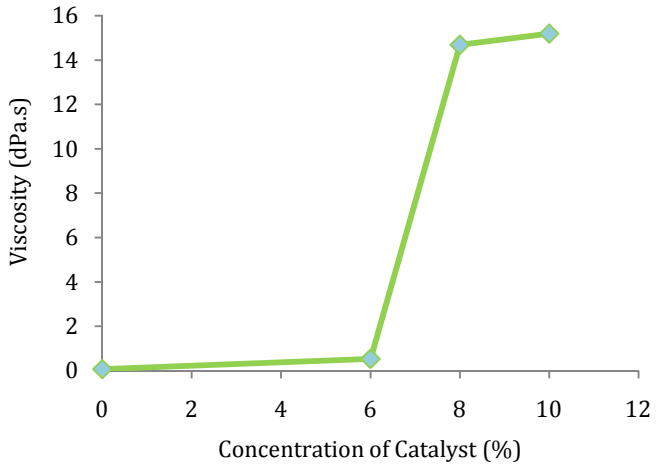

Figure 8. Effect of Concentration of Catalyst on Viscosity of Polyester

Figure 8 showed that viscosity increase with increasing in concentration of catalyst. Increasing in concentration of catalyst, the viscosity would increase with increasing molecular weight simultaneously [12]. This condition occured because of reduction of carbon bond in polyesterification and increasing viscosity in the media reaction at high concentrations. This double bonds cause a reduction of barriers on fluid flow in viscotester

which led to the appointment of the larger viscotester value [19]. This result was suitable for this research.

IV. CONCLUSIONS

The conclusion that can be drawn from this research is the product of polyester from PFAD has physical properties that close to the commercial polyester has a good quality of acid value and can be classified in low molecular weight of polyester which is more suitable for the application of modified polyester. The synthesis of polyester reaction is a reversible reaction in which the acquisition of the product depends on the concentration of catalyst.

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