Synthesis Biolubricant By Esterification Of Castor Oil 
(Jatropha Curcas L-Oil) With Chlorate Acid Catalyst

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Abstract. Biolubricant is made by reacting vegetable oil with alcohol with the help of strong acid or strong base catalyst in the esterification process. The goal of this research is to know the flash point of bio-lubricant, and know its characteristics. This research is done by reacting Jatropha oil and methanol reactant with perchloric acid with a variety of reactant mol and variety concentration of perchloric acid as a catalyst with esterification time of 7 hours, after that it will be purified by a various method to get the desired result. Results in this research have the highest flash point on 26 °C and lowest on 242 °C; highest viscosity on 217 cP and lowest on 130, 5 cP at 40 °C. At other temperature, the best viscosity is 184,5 cP at 40 °C and 27,45 cP at 100 °C. Average pour point from this bio-lubricant is -18,8 °C. Almost chemistry compound of Biolubricant contains fatty acid 9,12-Octadecadienoic acid (Z, Z) with methanol resulting mono-ester compound 9-Octadecenoic acid (Z)-, 2-hydroxy-1-(hydroxymethyl) ethyl ester.

1. Introduction
Biolubricants are vegetable oils [1] which are usually made from palm oil, coconut oil, soybean oil, castor oil, and sunflower oil [2]. The advantages of bio-lubricants are non-toxic or damaging to the environment, safer in terms of flashpoint, constant viscosity, lower evaporation of mineral lubricants, lower emissions [3], and easily biodegradable. The opportunity to produce bio-lubricants made from vegetable oils is quite large in Indonesia, which is a tropical country, allowing for the availability of raw materials. Indonesian have castor oil production in 2009 reached 8,013 tons from an area of 69,315 [4], [5].

2. Related Works
Biolubricants can be made using esterification and Trans esterification methods with basic ingredients of vegetable oil and alcohol with the help of catalysts with mixing methods at certain temperatures. Some previous studies stated: the use of castor seed oil raw materials with HCl catalyst obtained from the flashpoint was 302°C [6] with KOH catalyst the flashpoint results were still relatively low at 193°C [7] and sulfuric acid catalysts obtained 88% conversion with 264°C flash point values [8]. The mechanism of making bio-lubricant using used waste frying oil through an esterification-transesterification reaction produces a flash point value of 278 °C [9]. So this research wants to use perchloric acid catalyst through castor oil esterification reaction [10] in a variety of catalyst and mol
variety of castor oil in order to obtain a high flash point value [11] and can be compared with synthetic lubricants [12] which are predicated in Indonesia.

3. Research Methodology
The materials used: Castor Oil from the Surfactant and Bioenergy Research Center - IPB Bogor, HClO4 (Merck), methanol (Merck), distilled water. The tools used: the three neck reactor, stirrer, and rotor, oil bath, Liebig condenser, Tachometer, Thermometer, pycnometer (pyrex), NDJ-85 viscometer, Abel Closed Cup Flash Point Tester, Pour Point Tester Model: SYP1016-1B.

4. Result and Discussion
4.1. Viscosity
Viscosity is a physical property [13] that occurs because of the interaction of molecules [14] in the fluid so that it can withstand fluid flow which can be expressed as an indicator of viscosity. Viscosity determines the ease of circulation of lubricants in the engine where the viscosity that is not too thick does not overload the engine when it is first turned on and the lubricant is not too runny when the heat engine can still be used as a lubricant.

The chemical properties of Esters are determined by the balance between the length of the alkyl chain and the functional group bound by Esther. The length of the alkyl chain triglyceride determines the viscosity (lubricity) of the lubricant due to the increase in molecular weight where bio-lubricant has a more stable molecular weight which causes the value of the viscosity index (VI) of vegetable oil is greater than mineral lubricant [9]. The length of the alkyl chain also influences the viscosity index, which is more linear and long, so that interactions between molecules are stronger with increasing temperature compared to branching chains. The longer the Alkyl Triglyceride chain, the viscosity and the Viscosity Index are higher.

| Sample | Mol Ratio (Oil: Methanol) | Catalyst | 25°C | 40°C | 100°C |
|--------|--------------------------|----------|------|------|-------|
| BL1    | 1:1 0,5                  | 540      | 184,5| 27,45|
| BL2    | 1:1 0,7                  | 554      | 196,5| 30   |
| BL3    | 1:1 1                    | 541      | 201  | 24   |
| BL4    | 1:1 1,5                  | 492      | 166,5| 25   |
| BL5    | 1:2 0,5                  | 523      | 208,4| 25,3 |
| BL6    | 1:2 0,7                  | 495      | 223  | 27   |
| BL7    | 1:2 1                    | 546      | 197,5| 25,2 |
| BL8    | 1:2 1,5                  | 580      | 217,75| 26,25|
| BL9    | 1:4 0,5                  | 579,5    | 208  | 25   |
| BL10   | 1:4 0,7                  | 492      | 217,25| 22   |
| BL11   | 1:4 1                    | 518,5    | 130,5| 25,25|
| BL12   | 1:4 1,5                  | 523      | 175  | 24,75|
| Castor Oil |               | 576      | 202  | 29   |
| Fastron Semi-Synthetic SAE 20W-50 | -  | 151  | 16,9 |
| Prima XP SAE 20W-50 | -  | 164  | 17,66|
| Mesran SAE 20W-50 | -  | 153,12| 16,69|

From table 1, the higher the temperature made the smaller the viscosity value. Esters as bio-lubricant are more stable in viscosity than triglycerides. The heating process causes short chain oil to evaporate, leaving behind a long chain of oil. This is reinforced by the GC-MS analysis of bio-lubricant samples which produced 66% esters and dominant compound 9-Octadecenoic acid (Z) -, 2-hydroxy-1- (hydroxymethyl) ethyl ester.
From Figure 1 shows if the value of bio-lubricant viscosity is relatively lucrative. The difference in the value of viscosity in each sample due to differences in the composition of the esters formed was seen as a product yield from the difference in the ratio of moles of reactants and differences in the concentration of catalyst used. The heating causes short-chain fatty acids (low molecular weight) to evaporate during the reaction process. The high content of esters formed causes higher viscosity than commercial lubricants.

4.2. Flash Point Analysis and Pour Point

Flashpoint is a number that states the lowest temperature of fuel oil which will cause a momentary ignition. A high flash point will facilitate the storage of fuel because the oil will not be easily burned at room temperature. Whereas for pour point is a test for the lowest pour point of the oil. Pour point is used as a measure to what temperature the liquid fuel (oil) can still flow if cooled under predetermined conditions [11], [15].

Table 2. Flash Point dan Pour Point Product Biolubricant and Commercial Lubricants

| Sample             | Flash Point (Celsius) | Pour Point (Celsius) |
|--------------------|-----------------------|----------------------|
| Bahan Baku         | 242                   | -17.3                |
| BL 4               | 260                   | -18.8                |
| BL 7               | 268                   | -16.8                |
| BL 10              | 242                   | -16.6                |
| BL 12              | 250                   | -18.9                |
| Fastron (20W-50)   | 226                   | -30                  |
| Prima XP (20W-50)  | 227                   | -27                  |
| Mesran (20W-50)    | 225                   | -27                  |

The results of the synthesis of bio-lubricant of several samples indicate that the flashpoint value has increased from the raw material, and has a higher flash point value than the flash point value of the
lubricant commercial. From table 2. The flash point of raw materials has a temperature of 242 °C which when compared with commercial lubricants has a higher value than the specifications of Pertamina Lubricants likes: Fastron (20W-50), Prima XP (20W-50) and Mesran (20W-50). The BL10 sample has the lowest value of 242 °C while the highest value is obtained from the BL7 sample which is equal to 268 °C. Flashpoint is very closely related to the content of chemical compounds in it. The higher the molecular weight of the compound in bio-lubricant, the greater the energy needed to break the bonds. If a bond has broken into a low molecular weight compound, it will become flammable when passed through the fire.

The pour point value of each sample is still quite high. The best results from synthesis show pour point values from BL4 and BL12 samples of -18.8 °C and -18.9 °C in sequence. This is already quite good because synthesizing can change the composition of fatty acids into esters and reduce their pouring points. And it is also directly proportional to the viscosity which thickens at lower temperatures. However, the high pour point is the focus of this bio-lubricant because it is not good for areas with extreme winter like subtropical areas and additives need to be added if it will be used in the area. GC-MS Analysis;

| Table 3. Results of GC-MS Castor Oil analysis and Biolubrication Product |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| No | Compound | Area % | Similarity | Compound | Area % | Similarity |
|---|----------|--------|-------------|----------|--------|-------------|
| 1 | 9,12-Octadecadienoic acid -2-hydroxy-1- (hydroxymethyl)ethyl ester | 5.18 | 99 | 9,12-Octadecadienoic acid (Z, Z)- 2,3-dihydroxypropyl ester | 9.66 | 95 |
| 2 | 9,12-Octadecadienoic acid | 2.89 | 53 | 9,12-Octadecadienoic acid (Z, Z)- 2-hydroxy-1- (hydroxymethyl) ethyl ester | 2.84 | 72 |
| 3 | 13-Hexyloxacyclotridec-10-en-2-one | 1.16 | 52 | 9-Octadecenoic acid (Z), 2-hydroxy-1-(hydroxymethyl) ethyl ester | 66.47 | 49 |
| 4 | 2H-Pyran, 3,4-dihydro-6-methyl | 4.61 | 22 | 9,12-Octadecadienoic acid (Z, Z) | 3.51 | 50 |
| 5 | 9,17-Octadecadienal | 1.06 | 70 | Methyl 9,12-heptadecadienoate cis-7,cis-11-Hexadecadien-1-yl acetate | 1.12 | 87 |
| 6 | Benzene, 1-(chloromethyl)-4-(2-propenyl) | 1.4 | 43 | 1-Butene, 4,4-dichlorohexafluoro | 1.29 | 44 |
| 7 | 2-Methyl-Z,Z-3,13-octadecadienoic | 76 | 40 | 9,12-Octadecadienoic acid (Z, Z) | 3.96 | 35 |
| 8 | 10,12-Hexadecadien-1-ol acetate | 7.62 | 44 | 9,12-Octadecadienoic acid (Z, Z) | 11.07 | 64 |

At Table 3. the oil content of castor oil is 94.74% consisting of: 9,12-Octadecadienoic acid, 13-Hexyloxacyclotridec-10-en-2-one, 2H-Pyran, 3,4-dihydro-6- methyl, 9,17-Octadecadienal, Benzene, 1-(chloromethyl)-4-(2-propenyl), 2-Methyl-Z, Z-3,13-octadecadienoic and 10,12-Hexadecadien-1-ol acetate. With the largest amount in compound 2-Methyl-Z, Z-3,13-octadecadienol at 76%. While biolubricant products contain esters of 78.97% consisting of: 9,12-Octadecadienoic acid (Z, Z) - 2,3-dihydroxypropyl ester, 9,12-Octadecadienoic acid (Z, Z) - 2-hydroxy-1 - (hydroxymethyl) ethyl ester and 9-Octadecenoic acid (Z), 2-hydroxy-1- (hydroxymethyl) ethyl ester.

Castor oil can be modified into a lubricant by converting the group into esters. The reason Esters can be used as bio-lubricant because esters have unique properties that have good properties at low temperatures. This 78.97% content is a BL10 sample test result. The design of the reaction that might occur between 9,12-Octadecadienoic acid (Z, Z) with methanol produces a 9-Octadecenoic acid (Z), 2-hydroxy-1- (hydroxymethyl) ethyl ester compound can be described:
The results of the analysis show that the bio-lubricant synthesis produces a mono-ester compound but still contains a hydroxy group. Mono-Esters compounds from castor oil must still be modified because there are still two reactive groups namely OH (hydroxyl) groups. Alkaline hydroxyl groups require acids to form tri-esters [9].

The synthesis results in this Long chain ester compound which greatly influences the physical and chemical properties and the tribological properties of the lubricant. The longer the chain substituted into the middle part of the chain of an ester will have a positive effect on pour point, cloud point, and freezing point. If the main ester chain is extended, it will increase the steric resistance, thus inhibiting crystal formation and consequently will reduce the pour point and will increase the anti-wear opposite the temperature onset [16] [17].

5. Conclusion

From the results of the research made, the researcher can draw conclusions include:

1. Flash Point from bio-lubrication is obtained at 268 °C
2. The characteristics obtained from the best bio-lubricant are as follows:
   a. The mole ratio of castor oil: methanol is 1: 1
   b. Bio-lubricant was 184.5 cP at 40 °C and 27.45 cP at 100 °C
   c. The pour point of bio-lubricant is -18.8 °C
   d. The catalyst concentration used was 0.5 M
3. There is a fatty acid content 9,12-Octadecadienoic acid (Z, Z) with methanol produces 9-Octadecenoic acid (Z) - 2-hydroxy-1- (hydroxymethyl) ethyl ester compounds [18].

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