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Utilization of Byproducts from transesterification of waste vegetable oil as a source of polyol in making polyurethane adsorbents

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Abstract

The objective of this research is to make polyurethane adsorbent using glycerol from Waste Vegetable Oil. It is transesterified by using two steps. The first using methanol and KOH, the second using methanol and H_3PO_4 . Crude glycerol was purified by using the activated carbon. The analysis of glycerol and polyurethane was done by functional group analysis using FTIR spectrophotometer. The FTIR test of the glycerol from Waste Vegetable Oil showed that the presence of hydroxyl and hydrocarbon group are in 3379 and 2939 cm^{-1} also the resemblance of the spectra between standard glycerol to the resulting glycerol. FTIR test of the polyurethane showed that reduction the intensity of isocyanate group on number 2276 cm^{-1} from the MDI, thus indicating the formation of urethane groups. Based on swelling degree test, polyurethane with glycerol 10% resulting a high absorbency, it indicates that polyurethane is good adsorbent.

Keywords: transesterification, waste vegetable oil, glycerol, polyurethane, adsorbent.

Introduction

Waste Vegetable Oil (WVO) is a residual oil from the frying food. Vegetable oil can be produced from coconut plants and can also come from oil palm plant (*Elaeis guineensis*), which includes family palmae. Vegetable oil derived from palm oil tends to be preferred over vegetable oil from coconuts because it has several advantages among others such as lower smoky trends and fewer cultivation levels in the cauldron. Palm oil consists of glycerol compounds and fatty acids in the form of triglycerides (Suleman, 2012) ^[12].

Fatty acids bound in palm oil consist of saturated fatty acids and unsaturated fatty acids. The largest compilers of fatty acids bound to palm oil are palmitic acid 48%, 38% oleic acid, and 9% linoleic acid (Suleman, 2012) ^[12]. WVO is still considered a waste by some people. The number of exploration conducted to find alternative energy, making WVO began to be sought its usefulness. One of them is as raw material for making biodiesel (Aziz, 2008) ^[3].

The production of biodiesel or transesterification reaction of WVO is produced by glycerol byproduct with low purity level, commonly called crude glycerol. This product is produced about 10-20% of the total product volume (Darnoko, D and Cheryan, M., 2000) ^[5]. In 2010 Indonesia produced about 1.24 million tons of biodiesel. The amount of biodiesel that produce crude glycerol about 124,000 - 248,000 tons per year. So far, the resulting crude glycerol has not been utilized by the biodiesel producing industry, because of the amount of impurities found in the crude glycerol (Appleby, 2005) ^[1].

Crude glycerol can be obtained by several methods through transesterification reactions, saponification and oil hydrolysis. Preparation of glycerol by hydrolysis may be carried out with the assist of a catalyst or without a catalyst. This hydrolysis reaction is a reversible reaction and tend to be slow so the conversion tends to be low (Aziz, *et al.*, 2013) ^[4]. The saponification reaction of the oil requires KOH to obtain glycerol and this method requires considerable cost. In addition, the preparation of glycerol by transesterification can be done by reacting WVO and methanol using a KOH catalyst. Previous studies conducted by Arita *et al.* (2008) ^[2] indicate that acid catalyzed esterification may be used in low-grade crude oil or high free fatty acids, this method is more appropriate in the transesterification of vegetable oil.

The decreasing benefits and the economic value of glycerol poses a challenge to us to use them to be efficient products. Several studies have been conducted to increase the value of benefits and economics, that is the conversion of glycerol through chemical reactions such as selective oxidation, hydrogenation, polymerization, etherification, and with the help of microbes, namely fermentation. Rahayu (2012) [7] converts glycerol to polyhydroxybutyrate by using bacteria but the weakness is in the difficulty of cultivating bacteria. Sutiani *et al.*, (2004) [13] performs the manufacture of polyurethane-based glycerol adhesives producing highly promising products.

Polyurethanes are multifunctional materials, where their function depends on the polyurethane component. According to Rohaeti and Suyanta (2011) [8], that the use of ethylenediamine (polyol) can increase crosslinking so it can be applied as a raw material in the manufacture of plastics that can be degraded by bacteria. If it is assumed, flexible polyurethane foams that have many crosslinks, indicating that the polyurethane pore size will be smaller then it can adsorb (on the outer surface of the adsorbent) large organic compound. Based on the above explanation, the researcher is interested to do research about the manufacture of polyurethane adsorbent by using glycerol byproduct from the transesterification reaction of the vegetable oil.

Materials and Method

The method used in this research is an experimental method. The research included sampling, sample collection and management, transesterification of walnut oil, polyurethane synthesis, functional group analysis using FTIR spectrophotometer, glycerol density determination using pycnometer and Swelling degree test.

Tools and Materials

Analytical balance (Mettler-AT 200), pH meter, water bath, glassware, thermometer, separating funnel, Hot plate with stirrer, oven, polyurethane synthesis tool kit, Rotary evaporator tools (Eyela), Spektrofotometer Fourier Transform – Infra Red (FTIR Shimadzu Prestige 21), WVO, KOH, methanol, phosphoric acid, activated carbon, methylene 4,4 diphenyl diisocyanate (MDI), polyethylene glycol (PEG) 1000, distilled water, standard glycerol.

Procedure

Transesterification of WVO

WVO is first filtered and taken 500 g and then heated to 110° C. KOH is dissolved in 250 ml of methanol. Waste oil is heated to 60° C, a KOH methanol mixture is added and stirred for 1 hour, after which it is left for about 8 hours producing biodiesel and crude glycerol. (Aziz, *et al.*, 2013; Sarma, 2017) [4, 11].

Purification of Crude Glycerol

Crude Glycerol added phosphoric acid (H₃PO₄) until pH = 6, formed three layers, glycerol layer separated from other layers. Crude glycerol that has been separated added by water and activated carbon (4%). The mixture is stirred for 30 minutes and left for 24 hours, after which it is filtered, then evaporated with a rotary evaporator to remove the residual methanol and water content. Further analyzed by using FTIR.

Polyurethane Making

At this phase a polymerization reaction at room temperature with a mole ratio of MDI/PEG 1000 is fixed with variations in

glycerol concentration used in polyurethane synthesis of 0, 10, 20 and 30%. Glycerol MJ 10% added with PEG 1000, then added with MDI inserted into a closed container, then stirring until homogeneous while flowed nitrogen gas to obtain viscous fluid. Furthermore, the viscous liquid obtained is introduced into the mold and allowed to harden. The polyurethane sample was put into the oven for 2 hours at 40-50° C before it was characterized (Rohaeti, *et al.*, 2003) [9]. Polyurethanes characterization was performed by swelling degree test to determine polyurethane absorption and polyurethane functional group analysis using FTIR spectrophotometer.

Swelling Degree Test

Swelling degree test is done by soaking polyurethane with water solvent for 24 hours then weighed and recorded wet weight and dry weight.

Result and Discussion

Result of Glycerol Functional Groups Analysis Using FTIR

The purified glycerol analyzed using FTIR. The result of pure glycerol analysis as comparator and glycerol (WVO) using FTIR can be seen in Figure 1.

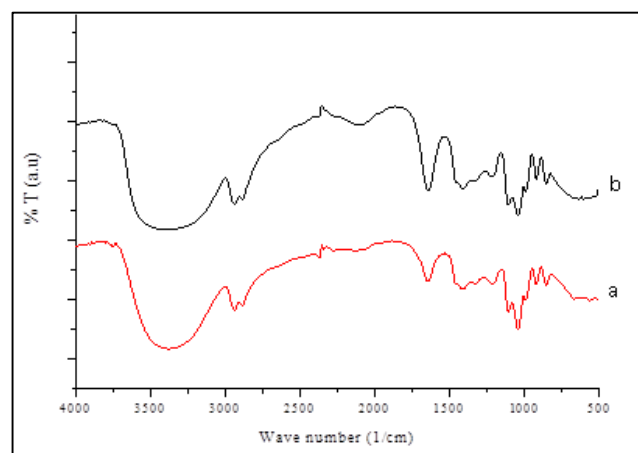


Fig 1: Spectra of FTIR a) WVO Glycerol and b) Pure Glycerol

Figure 1a. Showed that the transesterification byproducts of waste water indicated the presence of bands extending at a wave number of 3387 cm⁻¹ indicating the presence of OH (hydroxyl) groups. The absorption bands at 2939 and 2885 cm⁻¹ show the presence of aliphatic (alkyl) CH groups. From the FTIR spectra, it can be concluded that in the compound analyzed there is OH hydroxyl group, CH aliphatic, indicating that the presence of glycerol. Figure 1b. Showed that glycerol (standard) using FTIR showed a widening band at a wave number of 3402 cm⁻¹ indicating the presence of an OH (hydroxyl) group. The absorption bands at 2939 and 2885 cm⁻¹ show the presence of aliphatic (alkyl) CH groups. From the comparison of FTIR spectra of side-by-product gelsol from pure oil and pure glycerol, it can be concluded that in glycerol compounds of wetland oils analyzed there is OH hydroxyl group, CH aliphatic, indicating the presence of glycerol. (Syahputra *et al.*, 2015) [10]

Analysis of Polyurethanes Function Groups Using FTIR

Analysis of polyurethane functional groups using FTIR is done to determine the functional groups and the intensity of the resulting spectra of each material used. The results of this test to confirm that the synthesized polyurethane has been

successfully formed. FTIR spectra of polyurethane formation can be seen in Figure 2.

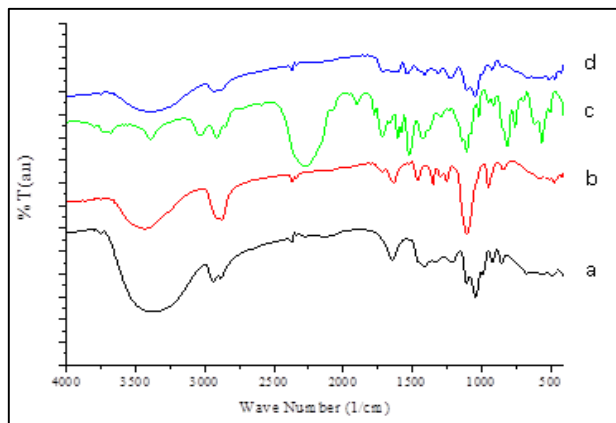


Fig 2: Spectra of FTIR a. Glycerol MJ, b. PEG 1000, c. MDI, d. Polyurethane

Figure 2a. Shows FTIR spectra of glycerol. This spectra contains the absorption of hydroxyl groups at 3356 cm^{-1} wave numbers which is also reinforced by the C-O range of 1141 cm^{-1} . In addition there is also C-H uptake at the wave number 2885 cm^{-1} . The spectra of FTIR of PEG 1000 is shown in Figure 2b. Figure 2b confirms the presence of hydroxyl group absorption at 3425 cm^{-1} waves, which is also amplified by the C-O range of 1118 cm^{-1} wave numbers and there is also C-H uptake at 2877 cm^{-1} wave

Figure 2c. Shows the FTIR spectra of the MDI confirming the presence of C = C groups of aromatic compounds shown in absorption of wave numbers 1658 cm^{-1} and clarified by the absorption of 3032 cm^{-1} wave numbers denoting = C-H. In addition, at the wave number 1720 cm^{-1} there is a C = O group. Furthermore, at the 2276 cm^{-1} wave number indicating the presence of the -NCO group and at the wave number 2916 cm^{-1} indicates the presence of a C-H group.

Figure 2d. Shows the spectra of the polyurethane synthesis results derived from a combination of glycerol, MDI and PEG 1000. Figure 2d shows the presence of successive amine groups (NH), C = O, CN and CO groups in numbers 3410 , 1635 , 1111 and 1041 cm^{-1} (Syahputra *et al.*, 2015; Jabbari and Khakpour, 2000; Yang *et al.*, 2012; Zhang *et al.*, 2012)^[10, 6, 14, 14-15] and reinforced by decreasing the intensity of the isocyanate group at the 2276 cm^{-1} wave number derived from the MDI thus indicating its formation Urethane group (-NHCO) (Ifa, *et al.*, 2008). Based on these criteria prove that polyurethane has been formed.

Result of Swelling Degree Test

This test was conducted to determine the absorption capacity of polyurethane wound bandage to water solvent and also to indicate the existence of cross link formed on the hard segment areas such as those observed by Rohaeti and Suyanta (2011)^[8]. The result of calculating the degree of swelling of the polyurethane wound dressing preparation is shown in Table 1.

Table 1: Results of Polyurethane Bloat Degrees

No	M ₁	M ₂	S (%)
PU0	0.0309	0.0390	26.21
PU1	0.0378	0.0754	99.47
PU2	0.0387	0.0683	76.48
PU3	0.0320	0.0386	20.62

In Table 1 it can be seen that the higher concentration of glycerol added by the absorption of water decreases, this is due to the increasing of crosslinking on the resultant polyurethane. This is in line with Jabbari and Khakpour (2000)^[6] stating that the more polyols are given the polyurethane will have a smaller or nearer pore. PU1 has a larger degree of bulk than the other sample of 99.47%. This suggests that PU1 has a higher hydrophilicity than other polyurethane products, thus indicating that PU1 can absorb fluid more effectively. Based on the results in Table 1, it is expected that PU1 has the optimum capability as an adsorbent.

Conclusion

Glycerol from transesterification of WVO can be used as a source of polyol in making polyurethane adsorbent, this is indicated by the presence of urethane group (-NHCO) in the FTIR spectra. The higher concentration of glycerol added, so the absorption of water decreases, this is due to the increasing crosslinks on the resulting polyurethane. PU1 has high adsorption capacity, so it is expected to be used as a good adsorbent.

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