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A Review on The Potential of Waste Cooking Oil-Based Polyol as A Polyurethane Precursor

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Reusing or recycling waste cooking oil (WCO) is an alternative to manage the abundance of WCO and sustain the environment. The main concern about WCO is how it will end up and how to overcome the problem of WCO and reduce WCO mainly from restaurants and homes. This paper aims to review and focus on the synthesis of polyurethane (PU)-based polyol via the hydroxylation of waste frying cooking oil. This study involves treating WCO for purification purposes and using different acids in the hydroxylation reaction to produce polyol. The purification of WCO includes heating, filtration, and treatment. The use of different acids, either formic acid or acetic acid, can improve the formation of WCO-based polyols in terms of the modification of the structure. The synthesis of PU from WCO is a great method to overcome the problem of WCO and a great way to sustain both renewable and non-renewable resources by reusing and recycling WCO.

Keywords: Waste cooking oil; palm oil; vegetable oil; hydroxylation; characterization, polyol.

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Palm oil is one of the generally well-known vegetable oils besides corn oil. Palm oil is mainly used in processing foodstuffs (68%) and cosmetics (27%), yet only approximately 5% are involved in other industries [1, 2]. Indonesia and Malaysia dominate the market segment with approximately 85% of the world market share as the major suppliers of palm oil [3]. Palm oil is widely used in the food industry as it is obtainable everywhere. It is also cheaper than other vegetable oils as Malaysia has abundant palm trees in each state. Used cooking oil from palm oil is classified as waste cooking oil (WCO) as it contains saturated fatty acids. The contamination risk of WCO can be reduced by reusing the oil to produce other products, including polyurethane (PU) precursors for PU synthesis.

A previous study reported on the use of residual frying cooking oil or WCO from soybean oil as a precursor for PU synthesis. This type of WCO has a good character in the formation of raw materials of PU. The pretreated WCO indicated the same organic structure as pure oil and can be used in the hydroxylation reaction by opening the oxirane ring to obtain polyols [4].

Polyol is a compound that contains abundant hydroxyl groups, which are being used widely in polymer manufacturing industries, especially for coatings, furniture, and adhesives. Originally, polyol is produced from non-renewable energy sources like petroleum. Due to the soaring price of petroleum, alternative sources must be discovered to conserve non-renewable resources and use safer resources. Polyols significantly affect the properties of the resulting polymeric material and product [5]. Polyurethane is a well-known polymeric material with various uses, such as foams, elastomers, adhesives, and fibers [6]. Polyurethane has good chemical and mechanical properties and is affordable; hence, the demand for PU is high.

This study is very important, especially for the environment because the abundance of WCO around the world might pollute the environment. Waste cooking oil can clog drains and also block sunlight and oxygen, killing living things in the ocean with the toxic waste oil. Waste cooking oil is bad for the human body and the environment as its nutrients and also physical and chemical compositions degrade during the usage of WCO. Its consumption can lead to severe health problems [7, 8].

This study discusses the significance of WCO pretreatment. This process will ensure that the polyol produced from WCO is free from any WCO contaminants. Then, the hydroxylation is proposed using two types of acids and also other alternative methods to synthesize polyols from WCO.

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This paper also studies the characterization of Fourier transform infrared spectroscopy (FTIR) analysis to prove the hydroxylation reaction, evaluate the functional groups present, and determine the wavenumbers of polyols and PU. The impurity of free fatty acid percentage (%FFA) was determined using ASTM D5555-95, and acid value (AV) was measured from %FFA to calculate the mass of potassium hydroxide (KOH) in milligrams needed to neutralize 1 g of chemical ingredient in the polyol. The hydroxyl value was determined using ASTM D4274-05. Meanwhile, the viscosity was measured using a Brookfield viscometer based on ASTM D4878-08 [4].

Pretreatment of Waste Cooking Oil

Sugarcane bagasse (SCB) treatment is one of the methods used to purify WCO from contaminants. According to a previous study [9], SCB and other lignocellulosic materials consisting of cellulose, hemicellulose, lignin, and a bit of extractive and mineral salts have the potential to become a reinforcement element in biocomposites. Sakdaronnarong et al. [10] mentioned that SCB is mainly used for single-step fractionation and hydrolysis with the presence of numerous organic solutions.

The fiber of SCB helps to reduce costs and contaminants in PU production [11]. This bagasse fiber is rich in huge parenchyma cells and vessel segments, which are good for low-cost adsorption and filtration [12]. Kerrou et al. [13] stated that SCB is cost-effective biomass for the production of adsorbent material, which can be achieved through various physiochemical processes. The adsorbent may be used on a large scale in industrial treatment operations.

Waste cooking oil contains mostly hazardous materials produced from the hydrolysis of triglycerides that yield free fatty acids (FFAs), diglycerides, monoglycerides, and glycerol, which can be indicated by the AV. The production of these components results in degraded oil quality and is harmful to the environment if the value is higher [14]. Hence, the use of activated carbon from bagasse can potentially reduce the AV and other impurities in WCO [15]. Tahir et al. [16] reported that the use of SCB reduced the viscosity of WCO from 106 mPa·s to 72.5 mPa·s due to the lower ring content of FFA adsorbed by the SCB. The color also changed from dark brown to yellow, making the WCO clearer than before. The analysis of the results in Table 1 shows improvement in the purification of WCO in terms of FFA content (%FFA), AV, viscosity, and color appearance.

Coconut fiber is a type of biomass waste that can be applied to produce activated carbon, and it is also known as coconut husk (CH). A study determined that pretreatment is necessary to increase the quality of the feedstock [15]. The adsorption utilizing activated carbon from coconut fiber is one of the approaches that can be used to reduce FFA content, and this approach is moderately simple and inexpensive. Coconut fiber can be utilized as a suitable feedstock to synthesize activated carbon as it consists of 64% cellulose and 22% lignin. Furthermore, it is also possible to synthesize solid absorbent using coconut fiber due to the high content of cellulose. The FFA content of WCO can be reduced using the activated carbon from coconut fiber in a batch process.

The use of CH instead of SCB in WCO pretreatment was previously reported [17]. A similar result was obtained, where the viscosity of WCO decreased, producing a lighter color. Similarly, the amount of FFA decreased from 4.4% to 1.4%, which is preferable in WCO pretreatment. The results of the WCO treated using CH-activated carbon are summarized in Table 2.

Table 1. Chemical compositions of untreated and treated WCO from palm oil using SCB[16].

Properties	Untreated WCO	Treated WCO
%FFA	4.4%	0.77%
AV	8.756 mg KOH/g	1.53 mg KOH/g
Viscosity	106 mPa.s	72.5 mPa·s
Color	Dark brown	Yellow

Table 2. Chemical compositions of untreated and treated WCO from palm oil using CH [17].

Properties	Untreated WCO	Treated WCO
%FFA	4.4%	1.4%
AV	8.756 mg KOH/g	2.786 mg KOH/g
Viscosity	106 mPa·s	97.8 mPa·s
Color	Dark brown	Light brown

Based on both studies, it can be observed that the WCO treated with SCB tends to have a lower percentage of FFA, which is 0.77% compared to the use of CH-activated carbon, which is 1.4%. Besides, the acidity of the WCO treated using SCB-activated carbon is also lower than those treated using CH-activated carbon. Therefore, it can be concluded that different activated carbons may provide different results in the values of viscosity and acidity. It should be noted that lower viscosity may ease the process of obtaining polyols.

Chemical bleaching is usually used in refining edible oil or oleochemical feedstock, where its implementation has already been accomplished. The technique is also used and applied in obtaining a light color precursor as it has the ability to remove the color pigment that exists in oils. The pigment is absorbed by the bleaching clay added during the process, where the amount of bleaching clay used may differ, depending on the type of oil and the desired color content. A study was conducted for WCO pretreatment via bleaching using hydrogen peroxide [18]. It was used as an oxidizing agent to remove the color of WCO. According to the study, the peroxide used achieved color removal of up to 55% efficiency, which is very effective even at a small loading.

The treatment with solvents, also known as solvent extraction, involves the use of lower molecular weight alcohols. This method did not effectively reduce the color of used cooking oil, with only a slight change in color, and the percentage of effectiveness was below 26% [18]. This is due to the non-polar nature of the coloring compound, which makes the alcohol less effective. Ethanol is able to yield higher removal efficiency than methanol and isopropanol, and this is contributed by the higher polarity of methanol that inhibits the removal of the color pigment. Another study also mentioned the importance of mutual immiscibility between the solvent and UCO to prevent losses of solvent, thus reducing the recovery cost [19].

Hydroxylation of Waste Cooking Oil

Acetic acid and hydrogen peroxide are well-known chemicals to produce polyols. Peroxy acids are typically applied in chemical treatment, production, and bleaching. According to Siwayanan [20], polyol manufacturing can be separated into three major processes: the response between glacial acetic acid and hydrogen peroxide to produce peracetic acid, palm oil epoxidation by peracetic acid, and the reaction of epoxidized palm oil and polyhydric alcohol to produce polyol. In addition, Unis [21] reported that hydroxyl radicals could react and destroy various types of organic impurities. Peracetic acid can be a reliable resource of hydroxyl radicals in the gas or solution phase with the addition of hydrogen peroxide.

According to Xu et al. [22], the hydrogen atom in the carboxyl group in carboxylic acid can offer its proton, which makes them acidic. It is a weak mono-protic acid in an aqueous solution and acts as one of the chemical reagents and catalysts in chemical industries. Due to the double bond in the chain, acetic acid is used because it is easy to break, and it is also the second simplest carboxylic acid after formic acid [23].

Fatty acids in palm acid oil are converted to peroxy acids by the reaction with hydrogen peroxide in the presence of formic acid. The peroxy acids are used for converting triglyceride double bonds to oxirane groups. Performic acid was used in the production of fatty acid methyl ester in soybean via epoxidation. The process was conducted at 40 °C with a substantial composition of hydrogen peroxide, which is 60 wt.% [24]. Formic acid plays a vital role in the formation of an oxirane ring, which is a catalyst and a reactant for the hydrolysis process. Formic acid is an ideal acid compared to acetic acid due to the oxygen atom that formic acid carries, which contributes to its great reactivity. However, formic acid is more expensive than acetic acid. Furthermore, formic acid can also be a viable carbon monoxide resource [25].

According to Ferraro et al. [4], formic acid has a greater influence on polyol production because it is stronger than acetic acid. Formic acid has two oxygen acceptor sites (i.e., hydroxyl and carbonyl) and two hydrogen bond acceptor sites (i.e., hydroxyl and formyl), hence providing various possibilities for hydrogen bond formation in the chain [26]. Besides, Madhu [23] mentioned that formic acid contains carboxylic acid attached to the hydrogen atom, and it is known as the simplest carboxylic acid.

Hydroxylation is a reaction where a hydroxyl group is added to a chemical mixture, and the hydrogen atom is covalently linked to the carbon atom of many molecules [27]. This reaction is carried out to produce polyol as a starting material for the synthesis of new products like PU. Hydroxylation usually uses peracids (acetic acid or formic acid) and a catalyst like hydrogen peroxide. The analysis to calculate the hydroxyl index of polyol is obtained from the FTIR spectrum. According to Ferraro et al. [4], the treated WCO was added to 3.0 moles of acetic acid and 1.5 moles of hydrogen peroxide for each mole of oil. Then, the mixture was stirred continuously at 40 °C. The early step was repeated by replacing acetic acid with formic acid in the same proportions prior to conducting the analysis using the FTIR spectrum.

Figure 1 shows the FTIR spectra of soybean oil and treated frying cooking oil before being tested with acetic and formic acid. A similar organic structure was obtained in the analysis with a slight difference in the range of 4000–650 cm^{-1}. Both oils are proven to have identical molecular structures.

Table 3 shows the FTIR transmittance values obtained from the FTIR spectra for the polyol synthesized with acetic acid and formic acid for groups -OH, C-O-C, and C=O. Figure 2 presents the FTIR spectra of treated frying oil after hydroxylation with acetic acid and formic acid. Figure 2 shows a huge difference between acetic acid and formic acid at wavenumber 3500 cm^{-1}. There are also differences in the peak signal from 1500 to 1000 cm^{-1}. The difference in the hydroxylation index for each polyol sample was recorded, and the highest index of mg KOH/g was obtained for the polyol synthesized from formic acid at 60 °C for 1 h. This is because formic acid is stronger than acetic acid for the hydroxylation reaction [4].

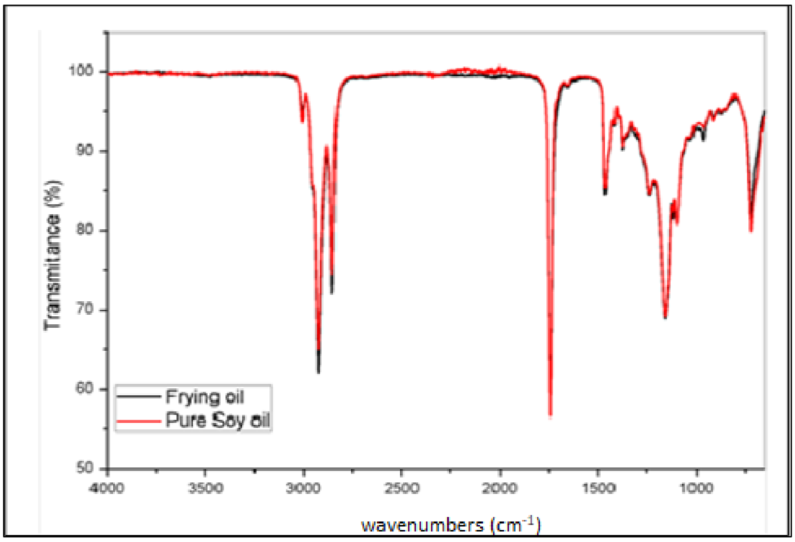

Figure 1. The FTIR spectra for soybean oil and treated frying oil [4].

Table 3. The FTIR transmittance values and hydroxylation index for the polyol synthesized from acetic acid and formic acid heated for 1 h at 40 °C and 60 °C [4].

	-OH	**C=O**	**C-O-C**	**mg KOH/g**
Sample	**Transmittance**	**Transmittance**	**Transmittance**	
Acetic Acid 60 °C/1 h	99	52	70	587.4
Acetic Acid 60 °C/1 h	98	53	69	586.3
Formic Acid 60 °C/1 h	94	52	57	593.0
Formic Acid 60 °C/1 h	94	53	57	591.5

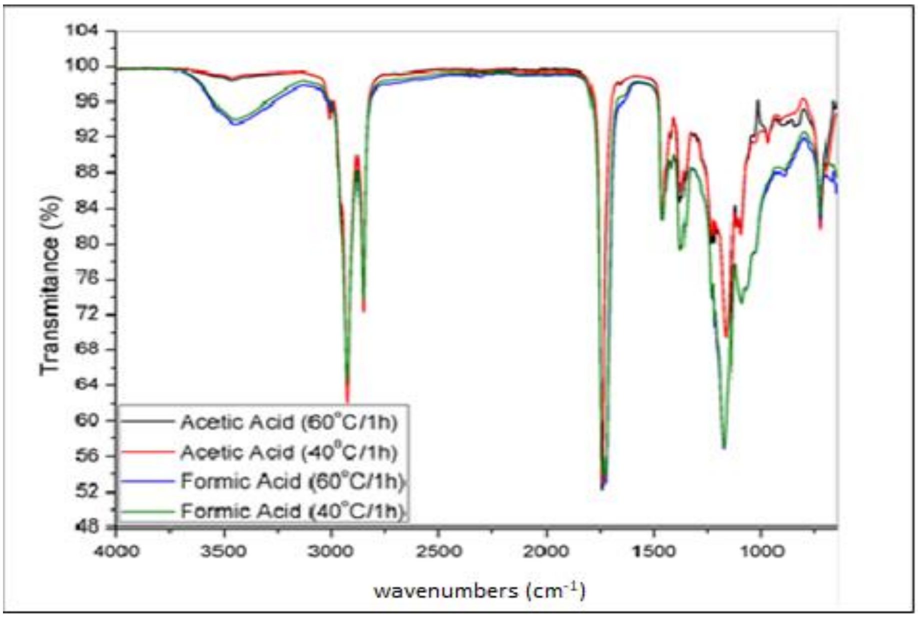

Figure 2. The FTIR spectra for WCO after hydroxylation with acetic acid and formic acid [4]

Waste Cooking Oil as a Polyurethane Precursor

According to Rihayat et al. [28], the hydroxyl groups from the epoxy open ring were produced by the hydroxylation reaction that occurred when the palm oil reacted with the oil oxidized by alcohol, catalyst, and water. The experiment was conducted in two stages for producing polyol, and the hydroxylation reaction was the second step to produce polyol, where the reaction introduced an OH compound in the chain. Methanol and glycerin were used in the experiment instead of formic acid and acetic acid to produce polyol. The study reported the formation of the N-H urethane group in PU at the absorption peak of 3374 cm^{-1}. Meanwhile, C=O urethane groups appeared at 1735 cm^{-1} and 2120–2180 cm^{-1}, thus indicating the formation of PU.

The products developed from WCO are being widely applied all over the world. Kurańska & Malewska [29] mentioned that PU products for coating and adhesive applications were produced from WCO in two-step processes. Waste frying oil as a raw material was reacted with acids to produce epoxides. These epoxidized forms of WCO would produce polyols when reacted with alcohols. Then, PU products were formed due to the reaction of polyol and isocyanate [30]. The biodegradability and other physical properties of PU products from WCO depend on the types of crosslinker or additive used, operating conditions, and WCO composition. A biodegradable PU sheet can be developed from WCO with the combination of polyethylene glycol and diphenyl-methane diisocyanate as reactants. The resulting PU sheets can also be mixed with fiberglass and silica, which can alter their properties, such as hardness.

CONCLUSIONS

Waste cooking oil can be recycled and reused to sustain the environment instead of throwing it away down the drain. Waste cooking oil has received a lot of attention and concern these days as it can bring harm to nature, humans, and even the sewage system. Various types of polyols can be synthesized from WCO via various reactions like transesterification, dihydroxylation, epoxidation, and hydroxylation. Polyol synthesis usually takes place in the ester linkage of fatty acid of WCO triglycerides. The hydroxyl group is introduced in the fatty acid linkage to produce polyol.

Although the WCO structure remains the same and changes slightly, the physicochemical properties will be affected. Properties like AV, hydroxyl value, and thermal properties will influence the properties of polyol. Therefore, it is important to ensure low acidity in WCO. Pretreatment is necessary to eliminate contaminants in WCO to obtain precise results for the polyol test, especially for PU synthesis. Finally, the type of acid and catalyst used for the hydroxylation reaction may affect the properties of polyol.

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