

Comparative Study on Optimization of Factors Affecting Epoxidation-Hydroxylation Reaction for The Production of Waste Cooking Oil Based-Polyol

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ABSTRACT

Raw materials for the production of polyurethane (PU), including polyols and isocyanate are derived from crude oils which pose a multitude of environmental impacts. While, the exploits of pure cooking oil, like palm oil used as a feedstock for polyol, could cause a bio-crisis, triggered by the imbalance of its demands and supplies. Hence, the utilization of vegetables or cooking oil from waste is mandatory to resolve the impacts. This study revolves around the comparative assessment of waste cooking oil (WCO) over pure cooking oil and the optimization of temperature, different acids, and catalysts, and hydrogen peroxide loading in the production of polyol via epoxidation and hydroxylation reaction. An acid reacts with hydrogen peroxide and produces peroxy-acid and water, which then reacts with WCO, the first step through the epoxidation process. Afterward, to produce polyol the breaking of the epoxidized-ring fatty acids is carried out by the reaction of hydroxylation aided by catalyst i.e., hydrochloric acid, sulphuric acid, or phosphoric acid. Notoriously, WCO has a similar triglyceride structure as pure cooking oil. However, even after filtration, some factors have a considerable effect on its fatty acid compositions such as duration of usage, exposure of temperature, and type of food used during cooking. Regarding temperature when producing polyol, it is discovered that higher temperature led to more ring-opening, nonetheless, prolonged high temperature causes more side reactions which are undesirable. Additionally, acetic acid has a surpassing oxygen carrier property over formic acid in epoxidation reaction.



Alongside, sulphuric acid is the most efficient inorganic acid catalyst due to stronger acid exhibits profound ring-opening of epoxidized oil. Furthermore, higher loading of hydrogen peroxide is preferable. Lastly, variations of extraction of sustainable acids which can be used as oxygen carriers for epoxidation i.e., formic acid and acetic acid derived from empty fruit bunch and food wastes are also demonstrated.

Keywords: Waste cooking oil; polyols; hydroxylation, polyurethane, environment impact.

INTRODUCTION

Raw materials for the production of polyurethane (*PU*), are polyols and isocyanate. Both materials are derived from crude oils which pose a multitude of environmental impacts. The concern derived from little fossil sources, energy demand, and global warming, which then led to the quest for more renewable polymer products with less carbon footprint [1].

While, the exploits of pure cooking oil, like palm oil used as a feedstock for polyol, could cause a bio-crisis, whereby triggered by the imbalance of its demands and supplies. Regardless, as long as the synthesis of polyurethanes from plant oils is controlled, the possible evocation of competition with food production [1] can be kept away for good. Major “bio-crises” triggered by the imbalance of demand and supply of biomass similar to the oil crisis when the oil supply was low in the 1970s, might occur if it is not issued correctly. Therefore, it is crucial to focus on exploiting agricultural and forestry wastes to avoid the conversion of rainforests and grasslands.

Used cooking oil has the same composition of fatty acid hydrocarbon chains as pure cooking oil. It remained the same even after undergoing heating and being exposed to other materials during cooking. However, the type of hydrocarbon chains present can be affected by cooking. It is important to filter and treat them, for the development of polyol. This is to prepare the fatty acids, to allow chemical derivation, specifically hydroxylation (ring opening). One of two ways making up the hydroxyl groups in the structure of the fatty acid, other than the trans-esterification

process. The process begins with a peroxy-acid (functional group) derived from a reaction between an acid and hydrogen peroxide then reacted with the waste crude oil, creating epoxidized *WCO*. Then, the hydroxylation process caused the ring opening of oxirane to be developed into polyol (increased hydroxyl content).

Hence, the utilization of vegetables or cooking oil from waste is mandatory to resolve the impacts. This study revolves around the comparative assessment of waste cooking oil (*WCO*) over pure cooking oil and the optimization of temperature, different acids catalysts, and hydrogen peroxide loading on the production of polyol via epoxidation and hydroxylation reaction.

Introduction to the synthesis of polyol

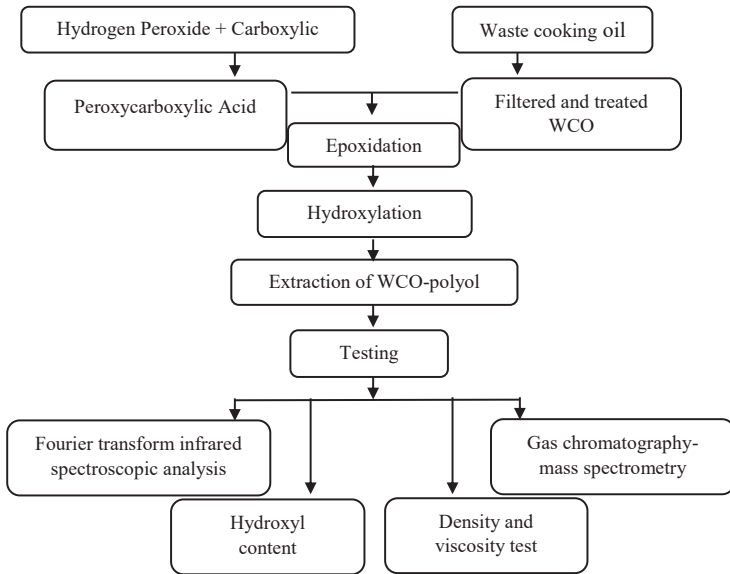


Figure 1: Reaction of epoxidation and hydroxylation of WCO [2]

In this research, the Conventional Chemical Treatment [2] a type of epoxidation process is the common approach used to synthesize a vegetable oil into a polyol. From Figure 1, the process begins with acid reacting with hydrogen peroxide to produce a peroxy-acid and water, which then

reacted with filtered and treated *WCO*, called the epoxidation process. The solution was stirred in a three-necked round bottom flask equipped with a filter funnel, magnetic stirrer, and water condenser, or in bulk at a certain temperature. After the addition of hydrogen peroxide is complete, in order to produce polyol, the breaking of the epoxidized-ring or ring-opening fatty acids is carried out by the reaction of hydroxylation aided by catalysts such as hydrochloric acid, sulphuric acid, or phosphoric acid at a certain temperature. In some case, alcohol such as methanol and ethylene glycol are used for ring-opening since inorganic catalyst like hydrochloric acid is incompatible with the epoxidized oils. The final products were extracted into petroleum ether and the ethereal layer was washed with aqueous sodium carbonate, followed by distilled water and sodium chloride solution. The ether layer was then dried over anhydrous sodium sulphate and ether was removed over a rotary evaporator at a specified temperature to gain the polyol. The analytical data to be determined from the *WCO*-polyol is the formation of *OH* (alcohol functional group) in the absorption peak of FTIR spectra. The absorption peak of *OH* is around 3300 cm^{-1} [3].

Epoxidation is preferred relatively because it increases the polarity and stability of vegetable oils and improves their compatibility with other polymers [4]. The epoxidation process occurs using per-acids formed in situ, which react to the carboxylic acid with concentrated hydrogen peroxide. As for its low cost, peroxy-acetic acid and peroxy-formic acid perform as an oxygen carrier was used [5].

Previously, the significant attribute of epoxidation is polarity. According to Gamage et al.[4], the polarity of vegetable oil increases with epoxidation. It was observed on the findings on Thin Layer Chromatography (*TLC*) analysis of some epoxidized vegetable oil, the more polar spend more time adsorbed on the polar silica layer coated aluminium (stationary phase). The reaction of a carbon-carbon of the double bond with active oxygen causes the addition of an oxygen atom, converting the original double bond into a three-membered epoxide of oxirane ring. Thus, the oxirane ring epoxides are highly reactive for the synthesis of a variety of chemicals such as alcohols (polyols), glycols, olefinic compounds, lubricants, plasticizers as well as a stabilizer for polymers.

Correspondingly, the polarity is associated with a number of physical properties that include, the solubility of the compound. In a sense of the thermodynamic idea for miscibility and compatibility, it is alleged that a smaller difference between solubility parameters indicates higher miscibility of the compounds [4]. The compatibility or miscibility between different polyols is expected to be an issue due to the different structures represented by each class of polyols. The end product of polyurethane would exhibit poor physical properties [6], however, can be enhanced by an epoxidation reaction.

This stepwise or two-step process namely epoxidation and hydroxylation have several viewpoints needed to be taken into consideration. Firstly, a high concentration of Lewis acid, for instance, hydrochloric acid used as a catalyst will cause unwanted side reactions like trans-esterification or cross-linkage [7] which would hinder the hydroxylation reaction. Likewise, another way to reduce the production of side products and ultimately produce a very desirable property of *PU*, the purification of the epoxidized oil also needs to be conducted. The purification process removes the spent acid and other impurities which are not completely eliminated. More importantly, the properties of polyols produced by epoxidation and subsequent oxirane ring-opening are dependent on several production variables such as feedstock characteristics containing different amounts of saturated and unsaturated components, as well as the types of ring-opening agents like catalyst and peroxide (oxidant). In most cases, the temperature and reaction time could also be a dependent factor in epoxidation and ring-opening of fatty acids.

Above all, although it is redeemed as a conventional method, it is preferable because it can be used as a preparation of different types of *PU* which can be conducted either in bulk or in solution, and controlling the final properties is unchallenging. There are more possible conditions or parameters to work with for this process. In order to produce the optimal or best results with further investigation and research which will be discussed, considering both derived from *CO* and *WCO*, specifically to improve the polarity of polyol and compatibility between polyol and isocyanate whereby link to *PU* physical properties.

Cooking oil (CO)

Cooking oil is a plant, animal, or manmade fatty acids used in cooking. Vegetable oils that were normally used for cooking, instead are used to generate the production of bio-polyol or natural oil polyols, primarily for the manufacturing of polyurethane (*PU*). It was promoted as an invention from the idea of “Green Chemistry”, described as a vegetable oil derived polymer used to replace petroleum-derived materials into more renewable and environmentally friendly materials [8]. Therefore, the natural oil polyols are considered sustainable, non-corrosive, and non-toxic. Realistically, the vegetable oils can replace petroleum derived polymers which are highly toxic [9]. In addition, it can be modified to a variety of applications. As it is highly processable, has different kinds of reactivity, functionalities, molecular weights, and properties that can be produced in a possible manner [10]. However, its price is relatively high thus its waste is utilized because it is a lot cheaper and environmentally friendly. The main compositions of *CO* as mentioned before, are fats and lipids which contain triglyceride molecules played a significant role in determining the quality of polyols and then *PU*. The degree of unsaturation content can be identified by its iodine value [11]. Unsaturation content is said to be high if the amount of double bonds or triple bonds within the chains is high.

Noted that, vegetable oils which have high contents of unsaturated fatty acids are oleic, linoleic and linolenic acids are very reactive to iodine, thus giving higher iodine value [11]. Generally, when higher iodine is attached to the oils it would give a higher value of iodine, meaning that it has a higher degree of unsaturation of the oils. As the increasing value of unsaturated molecules could be directed into effective collisions between reactant molecules when the reacting sites are higher [4], which serves as a site for chemical modifications. On the whole, a higher degree of unsaturation of *CO* which then undergoes the ring opening process produces polyols with a higher hydroxyl functionality. Hence, increasing the crosslinking density and tensile strength of *PU* derived from polyol and Methylene diphenyl diisocyanate, MDI [12].

The uniqueness of compositions of fatty acids in a matter of different sunflower oil, is shown clearly in Table 1. It was determined by a gas chromatograph (*GC*) mass spectrometer. Two types of sunflower oil from

different sources in South Africa were analyzed and as expected both have different compositions of saturated fatty acid (SFA), mono-unsaturated (MUFA), and poly-unsaturated fatty acid (PUFA) even though there are little differences in the total of saturated and unsaturated fatty acid total content. However, a characterization of fatty acid compositions of sunflower conducted by Orsavova et al. [13] showed a major difference in its value. One test of sunflower oil from the Czech Republic contains value of SFA with 9.4 %, and MUFA with 28.3 % meanwhile, PUFA with 62.4 %.

Table 1: Comparison between sample sunflower oil from South Africa and Czech Republic [14]

<i>Sunflower oil</i>	1	2	3
<i>Based country</i>	<i>South Africa</i>	<i>South Africa</i>	<i>Czech Republic</i>
<i>SFA (%)</i>	71.38	74.37	9.4
<i>MUFA (%)</i>	-	-	28.3
<i>PUFA (%)</i>	28.52	25.63	62.4

The major differences between South Africa and Czech Republic, have shown the fatty acid compositions of sunflower oils show diversity depending on the genotype and the region. In addition, climate conditions, especially high temperature and lower amounts of rain during the seed filling time, increases the unsaturation content (oleic acid) [14]. In other words, the compositions of the same type of *CO* cannot be standardized in a universal percentage and sunflower oil can be set as an example regarding this matter. Hence, it is advisable to determine the *CO*'s compositions before the synthesis of *CO* based polyol, to fully comprehend the direct connection between the composition of the feedstocks and the properties of the synthesized *CO* based-polyol. So that manufacturers or researchers can utilize the compositions of the *CO* for them to produce *CO* based-polyol according to desired properties of the designated application.

Table 2: Table of Fatty acid composition of soybean, corn and sunflower oil [15]

<i>Fatty acids</i>	<i>Palmitic</i>	<i>Stearic</i>	<i>Oleic</i>	<i>Linoleic</i>	<i>Linolenic</i>
<i>Soybean oil</i>	10.5	3.0	23.1	56.5	6.5
<i>Corn oil</i>	11.6	1.3	30.6	55.8	0.7
<i>Sunflower oil</i>	9.2	3.5	20.4	68.1	0.4

Cai *et al.* [15] studied the impact of the type of fatty acid found in soybean, corn and sunflower oil on its degree of epoxidation. Table 2 shows the compositions of the 3 samples, where the saturated acid component of soybean, corn and sunflower oil are 13.5, 12.9, and 12.7, respectively, whereas the unsaturated acid component are 86.1, 87.1, and 88.9, respectively. It was discovered that soybean oil had the fastest reaction rate which also increases the oxirane ring content. This is because, the highest amount of linolenic acid present in the soybean oil aids the chemical modification whereby the three-double bond (in linolenic acid structure) acts as a site for the peroxy acetic acid to react. Meaning, the higher the amount of linolenic acid or reactive site, the higher the reaction time. This can be supported by the fact that, even though sunflower oil has higher linoleic acid which is also an unsaturated fatty acid (consisting of two double bonds) than soybean oil and corn oil, it has the lowest oxirane content and almost the same reaction time as corn oil. Connecting the information, it can be directly seen that the increase in linolenic acid, increases the reaction rate as well as the oxirane content.

Then, the process will be continuing with hydroxylation of the epoxidized oil into polyol where this study will continue to assess or discussed the different variables affecting the epoxidation and hydroxylation process.

Waste cooking oil (WCO)

There are some researches based on the capability and suitability of *WCO* to *WCO* based polyol that has been done by previous researchers. The difference between *WCO* and *CO* compositions are elaborated in their study in relation to the factor that changes the compositions (%) of *WCO* after undergoing the cooking process. It is found that *WCO* could be degraded by heat and affected by the component of food used during cooking. However, it can still be used as the starting material because the compositions of the fatty acid are not affecting the further process like epoxidation and hydroxylation as much as it seems in the changes of chemical modification on its level of saturations (unsaturated and saturated fatty acid).

First and foremost, *WCO* is a sustainable material to produce biodegradable polyol. A promising ingredient to reduce carbon footprint since it originated from waste and a reusable means of manufacturing. It is important because, the use of *WCO* reduces the high production cost of biodiesel; solves problems associated with the disposal of *WCO*; eliminates problems associated with contamination of aquatic and terrestrial habitats and blocking of drains and pipelines as a result of inappropriate disposal methodologies; and generates additional income for households and small-scale businesses [16]. The best way to operate the production of waste cooking oil is first, the *WCO* are filtered and treated prior to synthesis of *WCO* into *WCO*-polyol. The *WCO* needed to be heated to remove the moisture and then should be allowed to cool to room temperature. For further treatment, the food residue is removed by the vacuum filtration process. Before it is used for the next process in synthesizing *WCO*-based-polyol, the filtered *WCO* should be kept in airtight conditions to avoid contamination. Then, the synthesis of *WCO*-polyol can be carried out by means of epoxidation and hydroxylation reactions.

The process of synthesizing the *WCO* into a polyol is similar to *CO* as a starting material. Based on an experiment conducted by Ferraro et al. [17], the authors used the same approach as when conducting the pure soybean oil to synthesize polyol by using waste cooking oil (*WCO*) specifically frying oil. The reason is because it is an abundant and underutilized raw material. Also, it has been proven that it has similarities in the organic structure of *WCO* to vegetable oil signified by FTIR. The treated frying oil proved to have a characteristic structure almost to the virgin soybean oil which is shown the functional group of polyols. Making the frying oil worthy as a starting material and suitable for the process.

To further support the success of this approach, a study conducted by Hasmaruddin & Mohd Tahir [18], proved that the epoxidation and hydroxylation reaction successfully converted double bonds in *WCO* structure into *OH*. The result from gas chromatography (GC) mass spectrometer analysis obtained indicated that *WCO* has successfully converted *WCO*-based polyol to a specified percentage of hydrogen peroxide. Whereby, showing the reaction is suitable for the synthesis of *WCO*-based polyol. Thus, *WCO* can potentially become a raw material of polyurethane.

Factors affecting properties of WCO

From research by Awogbemi *et al.* [16], four samples of *WCO* in Table 3, were used and their compositions were shown to have different attributes. The *WCO* samples were shown to have a fewer number of fatty acids and in smaller quantities with oleic acid as the most frequently occurring acid, appearing in all the samples. Some samples have more SFAs, and some have more MUFAs and PUFAs. The authors claimed that the usage and heating play an important role regarding the end compositions of *WCO*. Generally, the compositions of *WCO* can be affected by many factors.

Table 3: Amount of Fatty Acids Content of four samples of Waste Cooking Oil [16]

Fatty acid	Sunflower oil	Sunfoil	Palm oil	Depot margarine
SFA (%)	71.48	74.37	12.3	40.92
MUFA (%)	-	-	11.45	-
PUFA (%)	28.52	25.63	76.25	59.08

Firstly, the composition of the *WCO* samples changes dramatically from one to another due to the effect of prolonged exposure to high temperatures. These examples can be set as evidence of the changes in the composition of sample *WCO* after repeated high-temperature cooking. According to the fatty acid composition of the four samples, samples of sunflower oil, supposedly having higher amounts of SFAs were converted to MUFAs after usage. Again, for the same reason, there is variation in the fatty acid compositions of the two samples, in spite of coming from the same brand of sunflower oil and used to fry potato chips. This is also connected to another reason, which is due to different duration of usage. Furthermore, food items such as fish and beef, greatly affect the fatty acid composition of *WCO*. There were two palm oils used for “fish and chips” and “sausages and chips” at different outlets which did affect the fatty acid composition of *WCO* [19]. The fish has more unsaturated oil compared to sausages thus giving the alteration of fatty acid composition. While sausages could also trigger a higher pH compared to fish that are more acidic than those beef and added with the effects of thermal degradation and contamination from the food items. It was explained that most of the *WCO* samples witnessed a reduction in pH because of usage.

Ultimately, it can be said that the act of heating the food items used during cooking could lead to a change in the composition due to thermal degradation and chemical modifications. According to Susheelamma *et al.* [20], the reason for the presence of hydrocarbons and polymerized derivatives of glyceride is because of the occurrence of repeated and high cooking temperatures. It can be difficult to predict the generation of cyclic and noncyclic hydrocarbon in *CO* during the cooking process. The varieties of reactions during cooking produce many unstable intermediate hydrocarbons, including the weak hydrocarbon bond. Apart from that, it causes an increase of peroxide value because the multiple high temperatures cooking stimulate water as a weak nucleophile as well as the heat mass transfer and induced oxygen has worsened the thermal oxidation. Thermal oxidation will lead to cooking oil decomposition and forms volatile compounds and various monomers and polymers [21].

Effect of temperature on epoxidation and hydroxylation reaction

A suitable temperature is needed to allow oxirane production and the conversion of oxirane content into hydroxyl content (polyol). Jalil *et al.* [9] said that the optimum reaction condition of moderate temperature is at 40 - 60 °C, using sulphuric acid as the catalyst. In contrast, Zaher *et al.* [22] research reported that the process of ring opening took place at a higher temperature which is more than 80 °C. Due to more complications are present in the epoxidation of vegetable oils since the epoxidized product can be more diverse (such as mono-, di- or tri-epoxides). The diversity of the fatty acid is dependent on the seed oil origin [23]. Thus, higher temperature promotes oxirane ring opening which is required to produce more hydrolyzed *WCO*. However, different oils will get a different outcome from the epoxidation reaction at a certain temperature.

An experiment with different temperature settings was carried out by Tung *et al.* [3] at 60, 70, and 80 °C. The three temperatures were at a constant setting of 2000 rpm stirring speed, the molar ratio of epoxidized soybean oil: hydrogen peroxide of 1:15, and the concentration of catalyst sulphuric acid was fixed at 8 wt.%.

Table 4: Outcome of Hydroxyl content of 60, 70 and 80 °C at different time [3]

<i>Temperature, °C</i>	<i>Hydroxyl content</i>		
<i>At (hr)</i>	<i>1</i>	<i>2</i>	<i>3</i>
<i>60</i>	<i>Lowest</i>		
<i>70</i>	<i>Lower</i>	<i>Highest</i>	<i>Highest</i>
<i>80</i>	<i>Highest</i>	<i>Lower</i>	<i>Lower</i>

As tabulated in Table 4, the outcome when the reaction was carried out at 60 °C, the oxirane content of polyol product remained high, because conversion into hydroxyl group was low. At 70 °C, the ability to open the epoxide group increases in the first two hours was almost the same but 80 °C has the upper hand with 292.98 mg KOH/g whereas at 70 °C with 273.21 mg KOH/g. Regardless, for the reaction in the next three to five hours, the hydroxyl group of the polyol product at 70 °C was higher than that at 80 °C [3]. This indicated that a higher temperature is preferable however at a certain extent of time specifically at the early stage. Higher temperature does not always mean better, to cut down the energy used for the process for optimization is necessary. Thus, a temperature of 70 °C is the optimal temperature setting in a condition of 3 to 5 hours of reaction.

Based on another research by Cai *et al.* [15], who worked on the kinetics of in-situ epoxidation of soybean oil, sunflower oil, as well as corn oil by peroxy-acetic acid, catalyzed by sulphuric acid demonstrated that the kinetic and thermodynamic parameters increase in the process temperature would also increase the rate of epoxide formation. This study further supported the reason that in the previous study at 60 °C it has the lowest conversion of oxirane content compared to at 70 °C and 80 °C. It is clear that, if the conversion of oxirane is low after undergoing an epoxidation reaction the conversion of hydroxyl by hydroxylation is hardly possible.

In addition, the highest hydroxyl value obtained by Hasmaruddin & Mohd Tahir [18] was 229.32 mg KOH/g using 35 % of hydrogen peroxide at 50 °C for epoxidation reaction and at a gradual increase of temperature until 80 °C for hydroxylation reactions. The obtained hydroxyl content from WCO based polyol was lower than by Tung *et al.* [3] which is around 300 mg KOH/g and above. This might be due to the conversion of oxirane content being low, to begin with, and the use of hydrochloric acid as a catalyst.

Also, as a precaution, a temperature set higher (accelerated) might cause an explosion because the epoxidation is highly exothermic. Not to mention, oxygen carrier like performic acid is also highly exothermic.

To sum up this supported the theory that a higher temperature is preferable, however, the optimal temperature is around 70 °C not higher than that.

Effect of oxygen carrier on epoxidation and hydroxylation reaction

The “peracids” are general oxidants classified as oxygen carriers, commonly with electrophilic properties which react best with electron rich substrates. Peroxy acid is an aliphatic C2-C18 peroxy carboxylic acid including peracetic acid, peroxy phthalic acid, peroxy oxalic acid, peroxy malic acid, peroxy maleic acid as well as peroxy fumaric acid (European Patent, 2011). However, peroxyacetic and peroxyformic derived from acetic acid and formic acid respectively, are the most common oxygen carriers used for the epoxidation process of CO and *WCO*. This is because both are found to be successful oxygen carriers devising the formation of an oxirane ring of fatty acids, cheap and highly efficient. Peroxyacetic acid (PAA) is very useful for the epoxidation of unsaturated fats due to it acts as an electrophile with high selectivity in reaction, which means it is reactive to make up oxirane. However, its reactivity is lower than peroxide. Whereas peroxyformic acid (PFA) is deemed very reactive even so it readily decomposes upon heating and explodes in a condition where it is rapidly heated to a temperature of 80 °C until 85 °C which is highly exothermic.

The reactivity of the peroxy acid is one of the concerns. The reason is that the reactivity can affect the epoxidation reaction of the *WCO*. The reactivity is determined by the electron withdrawing characteristic of the substituents. It is usual for a strong parent acid to attribute more reactivity to the derived peracid [23]. The lesser the reactivity, the more stable the peroxy acid is. The stability of peroxy acids will be higher as molecular weight increases. However, the unwanted side reaction might occur. On a note, not only the reactivity affects the epoxidation reaction of the *WCO*, but the concentration of the acid can impact the outcome of the reaction as well.

A comparison of the effect of acetic acid and formic acid as an oxygen carriers on epoxidation reaction has been studied by Dinda *et al.* [5]. Based on the research, the conversion started with a comparatively higher oxirane conversion of 67.5 % in the presence of performic acid while the peracetic acid had 55.7 % oxirane content. In spite of that, progressively the oxirane conversion decreased while the iodine value conversion increased. Whereas with peracetic acid, the iodine value conversion increased gradually but oxirane conversion increases gradually until it reached a maximum value of 77 %, continuing to decrease with time. Moreover, these results also showed the difference in maximum oxirane value between iodine value conversion and oxirane conversion. Performic acid was higher (with 21 %) than peracetic acid (with 14 %). This indicates that undesired products formed in the presence of performic acid were higher. Despite, the presence of peracetic acid having a slower rate of formation of oxirane, it has the optimized conversion to oxirane that was higher and served as a better oxygen carrier.

Peracetic acid acts as a catalyst or oxidant in the formation of an oxirane ring and as a reactant in the hydroxylation of the oxirane ring showing that the epoxidation rate increases as its concentration increases. At a high mole ratio of peracetic acid, the stability of the oxirane ring was very poor and the formation of α -glycol or polyol increased as the mole ratio increased. The maximum oxirane can be obtained by optimizing the level of concentration of peracetic. Within the experimental conditions of the experiment, the most favourable concentration of peracetic acid appeared to be 0.5 mole ratio [5].

Another research done by Jumain Jalil *et al.* [24] shows that the maximum yield of epoxide was achieved when formic acid was used as the oxygen carrier compared to acetic acid. This is because the high epoxide yield obtained by the immediate reaction between the performic acid formed with the C=C double bonds in the oleic fatty acid chain and the minimization of oxirane ring degradation. The formic acid has the ability to minimize oxirane ring-opening by preventing the deprotonation of performic acid. Though the minimization of the ring opening is not what is intended, it is contrary to the objective of producing polyol, where the ring opening of oxirane is necessary to produce hydroxyl. Hence, acetic acid is preferable to optimize the production of oxirane content.

Effect of catalyst on epoxidation and hydroxylation reaction

Epoxidation and hydroxylation are chemical processes that generate oxirane and then introduces the hydroxyl group into an organic compound and is highly dependent upon the use of a catalyst and its concentration. From oxirane, the hydroxylation process opens the epoxidized ring of the cooking or vegetable oil. It is predicted that the use of sulphuric acid will ultimately produce a higher conversion of oxirane and polyol. This is because, catalyst could increase the conversion of oxirane in the beginning of the process and then aid the reaction time of ring opening (hydroxylation). There are a few catalysts used for the hydroxylation process to produce polyol, for instance, hydrochloric acid, sulphuric acid, phosphoric acid, and nitric acid. It is shown that sulphuric acid can produce the highest conversion of oxirane content into hydroxyl content. This is because it functions better at lowering the activation energy that increases the rate of the reaction. Different catalysts will give different efficiency in a sense it follows the kinetics mechanism. It can be also affected by its loading or concentration.

There is a study of epoxidation of mahua oil by in situ using hydrogen peroxide as oxygen donor and glacial acetic acid as active oxygen carrier. Using two different inorganic acid catalytic which are sulphuric and nitric acid at moderate temperature range of 55-65 °C. The effects of these parameters on the conversion to the epoxidized oil were studied. It was found that sulphuric to be more effective in terms of conversion to oxirane in the synthesis of waste cooking oil-based polyol using one-pot epoxidation and hydroxylation reaction by Hasmaruddin & Mohd Tahir, [18], which also successfully converted double bonds in *WCO* structure into *OH*.

The effectiveness of catalysts was tested out with same concentration. The most effective are, sulphuric acid, phosphoric acid, nitric acid, hydrochloric acid are arranged in descending order. Higher temperatures and sulphuric acid concentrations found to be able to lessen the reaction time needed to reach over the maximum conversion to oxirane value and simultaneously increased the extent of oxirane ring cleavage to glycols which is in favour [5]. Based another study conducted by Abdullah & Salimon, [25], the most effective inorganic acid used catalyst, was sulphuric acid. Generally, stronger acid could lead to a ring-opening reaction, which is preferable. However, sulphuric acid is reported to be unsuitable for certain

oils due to the low yield of epoxide.

The oxirane content decreases as the hydroxyl content of polyol increases in time. At the highest being using 8 wt.% of sulphuric acid, which suggests higher than 8 wt% could minimize the hydroxyl content on the polyol obtained. However, with a lower amount of catalyst in this case 6 wt.%, the ability to form hydroxyl groups was in fact not efficient [3]. Thus, 8 wt% is the optimized concentration of sulphuric acid.

Effect of hydrogen peroxide loading on epoxidation and hydroxylation reaction

The hydrogen peroxide not only reacted with the carboxylic acid to epoxidize the vegetable oil but also could benefit from converting the vegetable oil into the compound of polyol. According to Dinda *et al.* [5], it can be observed that the formation of glycol increased as this ratio of hydrogen peroxide increased from 0.25 to 0.75 mole. Showing it is favourable along with our objective of optimizing the production of polyol from vegetable oil. Additionally, a study by Gamage *et al.* [4] regarding the epoxidation of a few vegetable oils and the hydrolyzed polymer with peroxy-formic acid, found that the hydrogen peroxide was consumed in the process of formation of peroxy-acid during the thermal decomposition. The use of an excess of 100 % mol of hydrogen peroxide of double bonds as a reactant can make up a 100 % level of epoxidation.

It was also found that the hydroxyl value increased as the concentration of hydrogen peroxide used increased. The result from GC-MS analysis of successfully converted *WCO*-based polyol (of 35 % H_2O_2), with functionality of 2.44 suitable for the synthesis of *WCO*-based polyol [18]. Hence, higher loading of hydrogen peroxide is better to produce polyol from *WCO* or *CO*.

Sustainable acetic acid extraction from food waste

There are a few ways to obtain sustainable acetic acid from food waste which can help to reduce the environmental impact posed by food waste. Past studies on the oxidation of various food wastes in supercritical water showed that acetic acid was a stable intermediate product for almost all organic wastes [26,27]. Five types of vegetables namely carrots, white

radish, Chinese cabbage, cabbage, and potato and starch were conducted under a hydrothermal two-step process in a batch experiment and continuous flow experiments. The results of the batch experiment show that the yields of acetic acid obtained from five vegetables were almost the same.

The two-step process consists of both a hydrothermal reaction without a supply of oxygen (the first reaction step) and an oxidation reaction (the second reaction step). It was shown that the acetic acid yield was greatly increased by the two-step process. During the experiment, batch experiments of selected waste vegetables were performed under the condition of 300 °C, 1 min for the first step, and 300 °C, 1 min, and 70 % oxygen supply for the second step, found to be the optimum condition for producing acetic acid in the case of using starch as test material. The highest yields of acetic acid from five vegetables were almost the same as those obtained from starch. Again, similar to the highest acetic yield acid and parameters were also obtained successfully using the continuous flow reaction system type of the two-step process [28]. This process is most likely to be useful for it to be developed as an industrial scale process.

Sustainable formic acid extraction from empty fruit bunch (EFB)

There are a few ways to obtain sustainable formic acid from EFB which can help to reduce the environmental impact posed by EFB. Formic acid, and FA production kinetics experiments were established in a pressurized stirred reactor. Palm oil Empty fruit bunch and water were added to the reactor with a ratio of 1:25. After that, the reactor was heated and sealed. After reaching the desired temperature, sulphuric acid catalyzed (1M) was incorporated into reactants. The reaction times started when the sulfuric acid catalyst was released into the reactor. In which the samples were taken during the 10, 20, 30, 45, 90, and 120 minutes reaction at 150, 160, and 170 °C. From the experiment, it was found that the highest FA was formed at a reaction temperature of 170 °C after 20 minutes of reaction which produces 0.031 mol/L and 46.6 % mol of formic acid yield [29]. This method could also be implemented industrially in a reactor.

CONCLUSION & RECOMMENDATION

The act of heating the food during cooking could lead to changes in the composition of the fatty acid because of the repetition and high cooking temperature and food item having affected the oil. It is difficult to predict exactly how the process of cooking affects a certain *WCO* without investigating its previous usage and duration of usage. However, *WCO* even after undergoing the cooking process could possibly produce a polyol, because of the amount of unsaturated fatty acid like linoleic and linolenic acid which is a reactive site for epoxidation is still available in its compositions. The success can be seen in several studies including the one-pot epoxidation and hydroxylation reaction whereby they successfully converted double bonds in *WCO* structure into *OH*. Most importantly, the optimization of the factors affecting epoxidation and hydroxylation reaction in producing high hydroxyl content is as follows: higher temperature (not exceeding 70 °C), peroxy acetic acid as an oxygen carrier, sulphuric acid as a most effective catalyst (concentration not more than 8 wt.%), and higher loading of hydrogen peroxide are preferable to produce more hydroxyl content.

In order to produce a high conversion of hydroxyl from the compositions of the *WCO*, it needed to be analyzed first. A good amount of unsaturation level or double bond is necessary for the epoxidation and hydroxylation reaction to take place. Also, for the *WCO* based-polyol to achieve the highest conversion, the required reaction time is about 4-5 hours. However, it can be minimized by a higher concentration of catalyst and oxygen carrier, not higher than recommended concentration. This is because the epoxidation reaction and performic acid are highly exothermic.

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