Manufacture of Canola-Based Polyols for Commercial Polymers

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Abstract

Issues related to terms bio-based, biodegradable, and sustainable products has agitated environmental alert from the destructive effects of petrochemicals and their derivatives. The use of occurring molecules from natural resources for the production of industrial polymers and polymeric intermediates has risen attention of academicians and industrial communities. The laboratory work has been scrutinized in years on synthesizing polymers from natural resources. Polyols have brought on markets to manufacture polymer products one of which was polyurethane. The Canola based-polyol was the product modification of triglyceride's natural resource for the polymers production prepared for wide applications. This study was aimed to determine the optimize of manufacturing canola based epoxide and canola based polyol.

Keywords
Canola based polyols, vegetable oils, natural resources, triglyceride

1. Introduction

Edible oils became the most attainable chemicals for manufacturing green products which in contrast to the depletable petroleum oil. The polyols from the natural resource for the preparation of polymer chemicals are priceless compared to petroleum-based polyester and the existing market are rapidly expanded.

Manufacturing polymers from vegetable oils triglycerides along with their different types of fatty acids attributes are linked to a glycerol molecule through ester groups. The reaction were initially introduce the hydroxyl (-OH) groups into carbon-carbon double bonds in the vegetable oils to be chemically reacted to peroxy acids. The reaction proceeds through an epoxidation step then resulted in an unstable oxirane ring by acids to finally obtain polyols which contained hydroxyl groups [1]. The transformation was involved in a manufacture synthetic pathway, where the reactions were not very selective as can be indicated from the by-products obtained. Applying conventional methods to producing polyols will not result in a significant hydroxyl group with desirable viscosity to be proceeded to urethanes or others polymers' products [2]. There are still some doubt toward the existence of a completely renewable-based polyol, where the OH groups formation from unsaturated triglyceride [3], are expected to be more reactive to isocyanates for instance to forming polyurethane. However, the utilization of renewables for polyol has reactivated interest to minimize the dependency on petrochemicals that are now in shortage. Several methods were employed to functionalize the less reactive, low molecular weight for the competitive bio-based polyols [4].

The requirement of polyols for bio-polymers product must supported by the proper methods for the high unsaturated double carbon bonds of vegetable oils. The existing methods has resulted hydroxyl number of commercial polyol an oxirane ring opening by alcohols with hydroxyl number 270–310 mgKOH/g of the soybean oil which limit the applicability as flexible polyurethane foam. The largest non-functional branches in saturated fatty acid have caused to reducing reactivity which in general will affect the final foam properties [5].

Polyurethanes (PURs) foams were acquired through the reaction of polyols and isocyanates[6]; [7], where the commercial of both are predominantly from petroleum. However, there are trends to materials usage based on renewable resources [8], such as starch, sugar, and lignin [9]; [10]; [11], where often the polyols from synthetics are inpart or entirely compensated by bio polyols.

Bio-based polyols from various vegetable oils such as palm [12], soy [13], linseed [7], rapeseed [12]; tung [14]; [15], and castor oil [16]. It can be achieved by an establishment of hydroxyl groups into the double bonds or ester bonds. The epoxides products followed by the opening ring of oxiranes by an active hydrogen atoms through several reaction ; hydroformylation, ozonolysis and hydrogenation, transesterification, and transamidation. The contrasting approach of modifying natural oils to bio-polyols has made the research on bio-polyols rich of references.

The structure of polyols has cogent influence on the final properties of PUR foams, which also depends on the foaming process [17]; [18].The addition of bio-polyols can be prepared for flexible and rigid PURs synthesis which changed both physical and chemical properties of PUR foams and resulted in a more systemized cellular structure [12]; [19]. Bio-polyols for flexible foams synthesis are usually have hydroxyl number in the range of 50–200 mg KOH/g [13]; [19]; [20]; [21], with higher apparent density. The foams with the inclusion of 15% of bio-polyol had almost twice the tensile strength, which are three times greater compressive stress at 40% strain compared petrochemical foams. The increasing of bio-polyols can affected to the increasing of foams' resilience [19] [12], more smaller cell sizes in the cellular images, and the foams mechanical properties as well as the apparent density. Bio-polyols of the rigid PURs foam synthesis usually required more highly hydroxyl numbers in the range of 250-400 mg KOH/g [22]. The rapeseed oil derivatives are possibly replaced petroleum-based PURs up to 80 wt% the products are beneficial for heat insulation, it indicated through the closed-cell structures. Using glycerol according to several references are proven as chain extender, crosslinkers which also performed as plasticizer during the polyurethane synthesis [23].

This study aimed to determine the optimize of manufacturing of canola-based epoxide and canola-based polyol from variables of concentration of acid catalyst, temperatures, and time of reactions. Identify the functional groups which governed the polyols molecular by the support of FTIR and NMR ^{1}H and ^{12}C. Forecasting the proceed products of the existing property.

2.Materials and Method

The canola oil was purchased from the local grocery store. Hydrogen peroxide (35%), sodium sulfate anhydrous, glycerol technical grade were reterieved from Harum Kimia Indonesia. Sulfuric acid 96% was obtained from Mekar Jati, Indonesia. $NaHCO_3$ and Na_2SO_4 from Harum Kimia Indonesia. The diphenyl methylene diisocyanate (pMDI was manufacture by Bayer Corporation, Germany), where the NCO contentment was 31.5 wt% with functionality 2.6 as administered from supplier.

2.1.Synthesis of Canola Based Epoxide

The epoxidation reaction in unsaturated triglycerides is an initial reaction that must be passed before the next reaction forms polyols. In the epoxidation reaction carried out on canola oil, the ratio of CH_3COOH and H_2O_2 was calculated by stoichiometry [24]. The reaction will proceed well using an sulfuric acid catalyst where the concentration variables are 1%; 1.3%; 1.5%; 1.6%; 1.7%; 1.9%; and 2% (v/v) it was done *in situ* with the volume of previous canola oil was 100 mL and the time of reaction was 100 minutes, then determined the oxirane number (mg KOH/g) of canola based epoxide.

The oxirane number was determined through milliliters of sodium hydroxide. A 2 gram sample was poured into 250 mL Erlenmeyer flask dissolved in neutralized 96% ethyl alcohol. Heat it if necessary, cooled to room temperature. Titrate with phenolphthalein end point with 0.1N sodium hydroxide solution [25].

2.2.Synthesis of Canola Based Polyol

The resulted canola epoxidized were added to a stirred with the mixture of epoxide to 1,2 diethylene glycol (glycerol) with the ratio1:5 (mol/mol) than added concentrated sulfuric acid of 1.5 (%, w/w) to investigate the hydroxyl number of polyols. The reaction was stirred continuously at 60^0C and 70^0C for 90;100; and 120 minutes [26]. Then optimized the formula. Certainly, a balance volume of ethyl acetate was added, the solution washed with water then the organic layer was washed with $NaHCO_3$ and brine, dried with anhydrous Na_2SO_4, filtered, and finally concentrated using an evaporator. Determined the hydroxyl number and acid number.

2.3.Determination The Hydroxyl number and Acid Number of Polyol

The acid number of polyol are usually used to ensure batch-to-batch uniformity, using correction factor for the true hydroxyl number. They were determined according to ASTM D4662 The multiple hydroxyl groups of polyols correlates to the amount of polyols according to ASTM E1899. The general scheme of the polyol synthesis depicted in Figure 1.

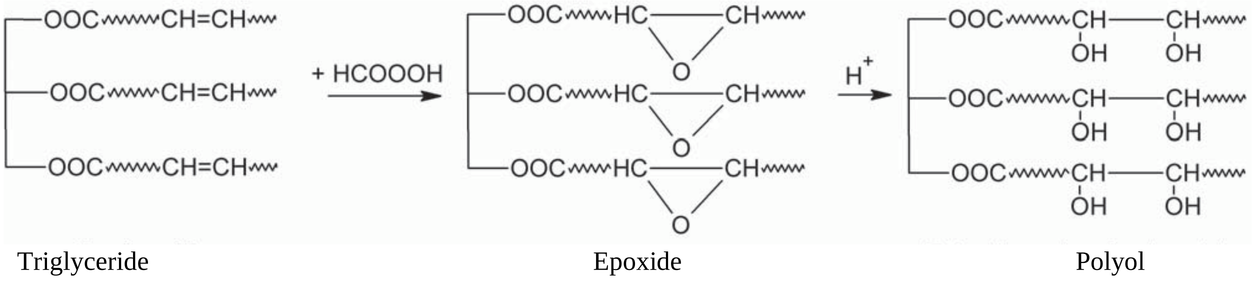

Figure 1. Scheme Manufacturing The Synthetic Pathway of Polyols from natural Canola Oil [7]

3.Result and Discussion

Characterization of Epoxide

For the ratio of CH_3COOH and H_2O_2 1/3.66 (mol/mol), the best concentration of sulfuric was 1.5% by weight with a temperature 60^0C in 100 minutes. This conditions has resulted the highest oxirane number, was 5.8 mg KOH/g, as can be seen in table 1. If the acid concentration increased to 2%

it initiates the solidification of epoxide product, as well as if the acid was increased up to 3% resulted the gel formation approximately 60% of the yield. If sulfur concentration below the best 1.5% , which was 1% and 1.3%, the oxirane number were not significantly different. The reaction time plays an important role for producing highest oxirane number, where 100 minutes produces high epoxide oxirane number than less 100 minutes for 100 mL of canola oil. Increasing the catalyst to 2% has forming an initial solidification of the epoxide, and this was becoming more worsen because the 60% gelling formation. The characterization were done by the support of FTIR and NMR by ^{1}H and ^{12}C.

Table 1. The effect ratio of CH_3COOH/H_2O_2 (1/3.66)(mol/mol) to
The Production of Canola Based Epoxide

CH3COOH/H2O (mol/mol)	% vol Catalyst	Temp. (deg C)	Time (Minute)	Oxirane (mg KOH/g)
1/3.66	1%	60	90	4.5
1/3.66	1%	60	100	5
1/3.66	1.50%	60	100	5.8
1/3.66	1.70%	60	100	5.4 5.3
1/3.66	2%	60	100	Initial solidification
1/3.66	3%	60	100	60% gel

If the ratio of CH_3COOH with H_2O_2 was increased to 1/3.74 (mol/mol) it was found that the concentration of sulfuric 1.3% (v/v) was not significantly different from 1.5% (v/v), where the number was around 5.7 mg KOH/g at the best temperature of 60^0C illustrated in Table 2. The acid number with the concentration of catalyst 1% was 2.4 and it was 1.1 with the catalyst 1.5%.

Table 2. The Effect Ratio of CH_3COOH/H_2O_2 (1/3.74)(mol/mol) to
The Production of Canola Based Epoxide

CH3COOH/H2O2 (mol/mol)	% vol Catalyst	Temp. (deg C)	Time (Minute)	Oxirane (mg KOH/g)
1/3.74	1.30%	60	100	5.7 5.8
1/3.74	1.50%	60	100	5.6 5.7
1/3.74	1.70%	60	100	4.5 4.5

If the ratio continues to be increased to 1/3.89 and 1/3.97, the best sulfuric concentration was when the oxirane value was the highest. It was found that the best acid catalyst concentration was 1.5% (v/v). At a ratio of 1/3.89, it was tried to increase the acid concentration to the level above 1.5% (v/v), the oxirane number was still in the range of 5.3-5.6 mg KOH/g. Another thing will be found if the temperature was increased to 70^{0}C though the concentration was 1.5% the oxirane tends to decline. Moreover the time extended 10 minutes from 100 minutes there were tends to continues declining, it was most probably the ketones formation. As can be summarized the optimum reaction condition was 60^{0}C, the catalyst was 1.5 (%,v/v), and the reaction duration was 120 minutes. It was shown in Table 3 and Figure 2.

The acid number of 1.5% catalyst concentration was 0.4 and was 1.1 with catalyst 2% for the ratio CH_3COOH/H_2O_2 (1:3.97) (mol/mol).

Table 3. The Effect ratio CH_3COOH/H_2O_2 (1/3.89)(mol/mol) to the Production of Canola based Epoxide

CH3COOH/H2O2 (mol/mol)	% vol Catalyst	Temp. (deg C)	Time (Minute)	Oxirane (mg KOH/g)
1/3.89	1.60%	60	100	5.3 5.3
1/3.89	1.70%	60	100	5.6 5.6
1/3.89	1.90%	60	100	5.5

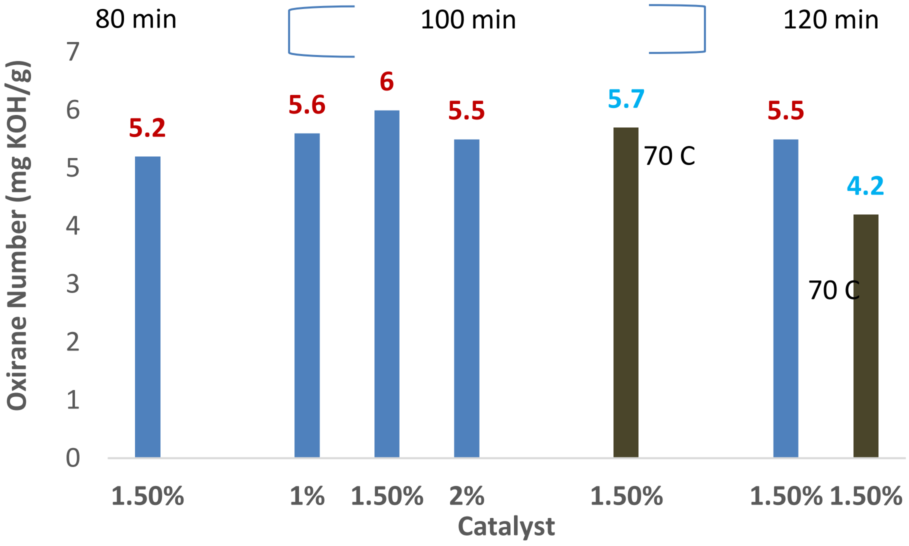

Figure 2. The Optimum Production of Canola Based Polyol at ratio of CH_3COOH/H_2O_2 (1/3.97)(mol/mol) at 60^{0}C . The reaction was done in 80;100; and 120 minutes.

Consequently, for commercial point of view utilization the natural-based polyols specifically canola based were commonly mixed with synthetic fossil-based polyols to attain an adequate foam properties. The reason was found, the primary alcohol in the polyols were usually three times more reactive to isocyanates than secondary alcohols [27], this can lead to by-product formation and become problems for the waste disposal and marketable materials [28].

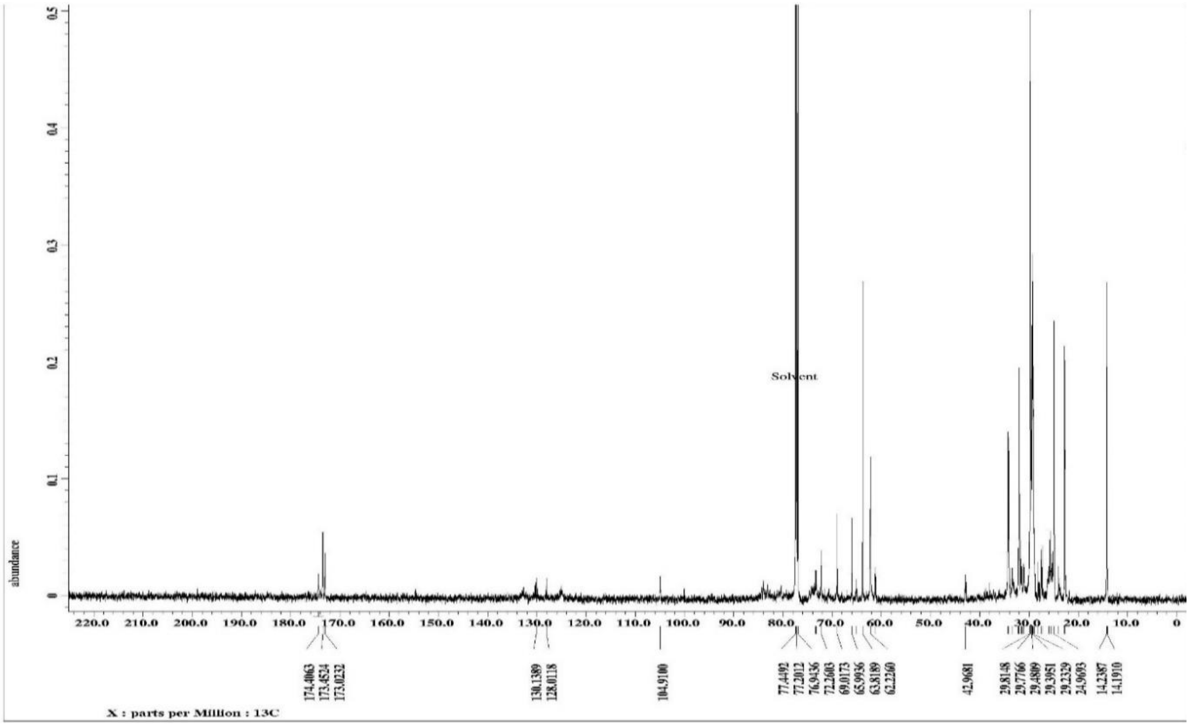

Figure 3. The ^{12}C -NMR of Polyol

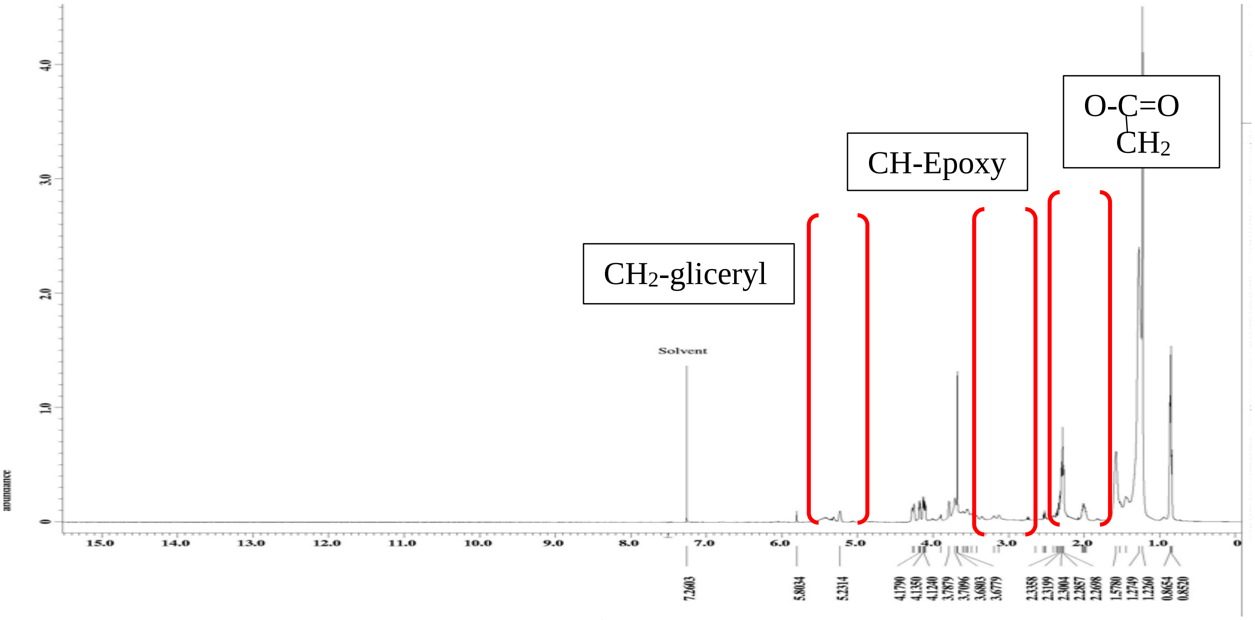

Figure 4. The ^{1}H-NMR of Polyol

The FTIR spectrum of the C=C bonds of the canola oil have been reduced. The absorption band centered at 3,300 cm^{-1} this was the characteristic of hydroxyl group, which has dissappeared in the saturated triglyceride, but appears in the other three samples with a tendency to grow in tremendously and extensively.

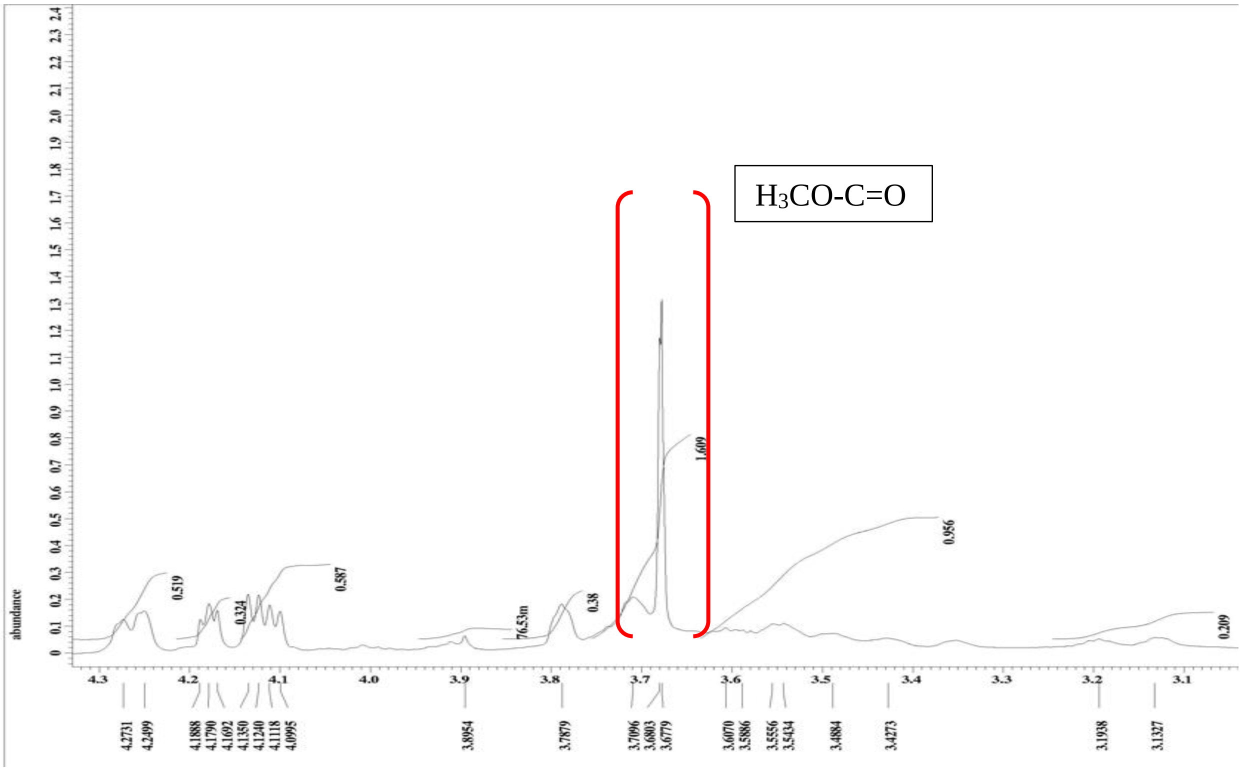

Figure 5. ^1H -NMR in Magnifying scale

The interpretation of the spectrum above as was
^1H-NMR (Chloroform D 400 MHz): d 5.23 (m, 1H, CHO- COR), 4.29 (dd, J = 3.7 Hz, 2.3 Hz, 2H, CH_2OCOR), 4.179 (dd, J = 6.0, 12 Hz, 2H, CH_2OCOR), 3.78 (t, J = 6.5 Hz, 4H, CH_2OH), 3.67 (t, J = 7.5 Hz, 6H, CH_2CO), 2.268 (m, 10H, CH_2CH_2CO and CH_2CH_2OH), 1.27 (m, 44H, CH_2), 0.865 (t, J = 6.5 Hz, 3H, CH3). ^{13}C-NMR (Chloroform D 100 MHz): d 174.4 (COR, sn-1, 3), 173.45 (COR, sn-1, 3), 170.1 (COR, sn-2), 69.01 (CHOCOR), 63.81 (CH_2OCOR), 62.22 (CH_2OH), 29.81, 29.77, 29.48, 29.39, 29.23,24.96, 14.23 (CH3). CI- MS: m/z 693.6 ([M+Na]+).

The optimized hydroxyl value of polyol was in the range 152.4± 0.3 to 176.4±0.5 mg KOH/g and the acid value was in the range 22.9±0.1 mg KOH/g[29]. The hydroxyl value also given information about degree of esterification. Acid value of polyol shows the presence of OH (hydroxyl) and grouping the type of foam (soft or rigid) from polyol if reacted to isocyanate. The high acid value will produces rigid vice versa.

Conclusion

In this study, the canola oil was employed for the production of polyol prepared for the commercial polymers. From the test results on polyols supported by data from FTIR, NMR ^{1}H and ^{12}C and the references the position of OH on the Carbon primer was more reactive to isocyanate which leading to the formation of by-products or in other words produces wastes. In terms of production costs, this will not be profitable so it was necessary to add petroleum oil to suppress this reactiveness.

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