Ozone-Mediated Polyol Synthesis from Soybean Oil

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ABSTRACT: Polyols from vegetable oils can replace petroleum-based polyols in the preparation of polyurethanes and polyesters in a wide range of applications. However, previous preparation methods are either too costly, inefficient, or yield secondary alcohols, which are less reactive than the desired primary alcohols. The objectives of this study were to prepare primary soy-based polyols by a new catalytic ozonolysis process and to characterize the composition of the product mixture. In this new process, the polyols were prepared by passing ozone through a solution of soybean oil and ethylene glycol in the presence of an alkaline catalyst. Unlike conventional ozonolysis that yields aldehydes and carboxylic acids by spontaneous decomposition of the ozonide intermediates, the ozonides in our method reacted with the hydroxyl group of the glycol to form an ester linkage with a terminal hydroxy group. Statistical analysis of the product mixture indicates that the resulting polyol mixture is more uniform than the original TG mixture, having (2-hydroxy)nonanoate as the major component of the new hydroxyl functional TG. The chemical structure of the polyols produced was further characterized by iodine number and ^{13}C NMR and FTIR spectroscopy, which confirmed the cleavage of the double bonds, the presence of hydroxyl groups, and the formation of new ester linkages.

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KEY WORDS: Ozone, polyol, soybean oil.

Soybean oil is an abundant renewable resource that can be used to manufacture of polyesters and polyurethanes provided it can be suitably modified to have alcohol groups in its structure. In addition to being a renewable resource, there are several other compelling reasons to use soy-based polyols as starting materials: The production of polyols from petrochemicals requires a great deal of energy, as oil must be drilled, extracted from the ground, transported to refineries, refined and otherwise processed to yield suitable polyols. Furthermore, the process itself is costly and adversely affects the environment. Thus, it is desirable to replace petroleum-based polyols with the more versatile, renewable, less costly, and more environmentally friendly biobased polyols. Several researchers have investigated incorporating alcohol groups into soybean oil and other FA TG derived from vegetables oils.

One of the early methods of preparing polyols from various vegetable oils was based on transesterification of the FA in TG with a polyol such as glycerol, glycerin, pentaerythritol, α-methylglucoside, or sucrose (1,2). Unfortunately, premature degradation occurs by this process as a result of high temperatures and a relatively long reaction time. Another method is based on reacting vegetable oils with peroxy acid to yield epoxidized FA. The epoxide rings are then opened (3,4) or hydroxylated (5) with polyfunctional alcohols to yield secondary alcohols. Epoxidized soy oil is available commercially, but the reactivity of this oil is low owing to the nature of the secondary alcohols. Furthermore, several hydroxyl groups per FA residue are obtained (at least from FA containing more than one double bond). Consequently, multiple numbers of hydroxyl groups having varying degrees of reactivity are present, which tend to complicate subsequent reactions and may lead to premature gelation. Hydroformylation offers another method to prepare polyols whereby aldehyde functional vegetable oil that is first obtained is then hydrogenated to alcohols (6,7). Polyurethanes prepared from these polyols had different mechanical properties, depending on the hydroformylation catalyst that was used. Thus, rigid materials at room temperature were obtained with a rhodium catalyst whereas cobalt-catalyzed hydroformylation led to rubbery materials (8). An alternative method to prepare primary polyols is based on oxidizing an olefin having a carbonyl group with molecular oxygen, followed by hydrolysis and reduction of the acetal (or ketal) to an alcohol (9). Although this method appears somewhat complicated and must be run at high pressure, good yields are reported. A somewhat less complicated method, also based on an oxidation process to yield polyols, is based on catalytic oxidation using an organic hydroperoxide in the presence of OsO_4 and a NaBr co-catalyst (10). An alternative process is to use ozone to cleave and oxidize the double bonds in the vegetable oil and then reduce the decomposing ozonides to alcohols using $NaBH_4$ or similar reducing agents.

Thus, there is a need to improve the chemistry as well as the process and to devise a more efficient method to prepare vegetable oils containing primary alcohols. Here, we report our initial efforts to synthesize such soy-based primary polyols in a single-step ozonolysis procedure. Our method takes advantage of the ease and efficiency of the oxidation methods mentioned earlier, and the synthesis is relatively simple and fast.

EXPERIMENTAL PROCEDURES

Materials and methods. Degummed soybean oil was purchased from Spectrum Chemicals (Gardena, CA) in a 20-L container and was used without further purification. Linoleic acid (purity >99%) was purchased from Eastman Chemical (Kingsport,

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TN). Ethylene glycol, sodium hydroxide, pyridine, 4-dimethylaminopyridine (4-DMAP), and $CaCO_3$ were purchased from Sigma-Aldrich (St. Louis, MO). Ozone (about 6 wt% in oxygen) was produced by passing dry oxygen (0.25 ft^3/min = 7 L/min) through a Trailigaz ozone generator (model number OZC-1001; Praxair, Cincinnati, OH). The ozone was introduced into the reaction medium as small gas bubbles by passing the ozone/oxygen stream through a fritted disc. The formation of these small gas bubbles improved the dispersion of ozone within the reaction medium. Any unreacted ozone was decomposed by venting the exhaust gas through aqueous KI solution. Unless noted, all ozonolysis reactions were run at 0°C and maintained at this temperature with an ice/water bath.

Reactions with model compound. Linoleic acid was used as a model compound for evaluation of the ozone attack on the double bonds. Linoleic acid (200 g) and ethylene glycol (180 g) were placed in a 500-mL reaction bottle and maintained at 0°C with an ice/water bath. Ozone was bubbled through the reaction medium, and samples were removed periodically and analyzed to determine the extent of double bond disappearance by iodine test as shown in Figure 1. The error bars in this figure were determined based on the variation in the iodine numbers of 5 repeated samplings.

Ozonolysis of soybean oil. Soybean oil (200 g), ethylene glycol (150 g), and various amounts of catalysts (NaOH, pyridine, 4-DMAP, or $CaCO_3$) were placed in a 500-mL gas wash bottle and maintained at 0°C in an ice water bath; ozone was then bubbled through the reaction mixture. Unless otherwise noted, all reactions were run for 2.5 h, and the product was washed 5 times with about 500 mL distilled water for each wash to remove any excess ethylene glycol and catalyst. (When a heterogeneous catalyst such as $CaCO_3$ was used, it was filtered out through a fine filter paper.) The product was then dried over molecular sieves for 48 h prior to testing. Typically, all ozonolysis experiments were replicated three times unless otherwise specified to verify the extent of the reaction and determine the experimental error associated with the process.

Characterization procedures. The hydroxyl number, defined as the number of mg of potassium hydroxide equivalent to the acetic anhydride consumed in the acetylation of 1 g of sample, was determined by ASTM test method D1957-86 (11). Hydroxyl functionality was derived from the hydroxyl number and is defined here as the average number of hydroxyl groups in 1 mole of TG. Thus, in using a typical composition of soybean oil as shown above with 4.6 double bonds per TG molecule, the maximum hydroxyl functionality is 9.2 since the cleavage of each double bond yields 2 hydroxyl groups.

The number of double bonds was determined using the iodine number test according to ASTM test method D1959 (12). The iodine number in this test is defined as the mg of I_2 per g of sample.

Functional groups were identified using PerkinElmer FTIR model 1000 using at least 64 scans. Before recording a spectrum, the sample holder was flushed with N_2 to remove moisture and CO_2 and the background was recorded. The spectra were obtained after polyol samples were dissolved in chloroform and a drop of the solution was placed on sodium chloride crystals. The solvent was allowed to evaporate leaving a thin film on the surface of the crystal. The sample cell was constantly purged with dry nitrogen while the signal was acquired.

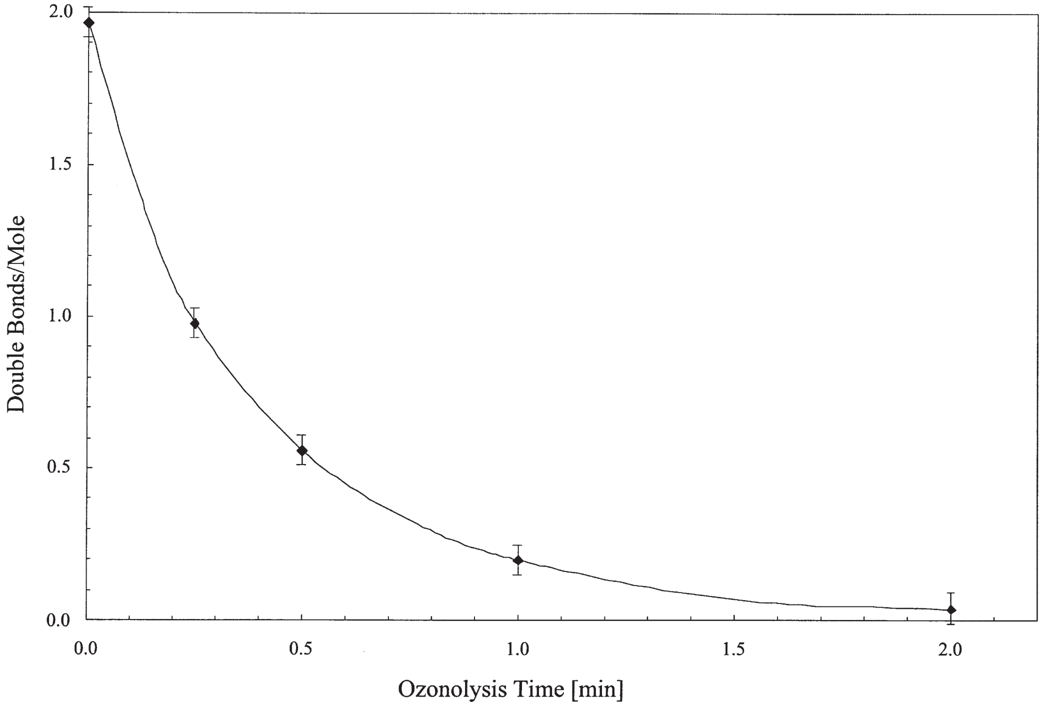
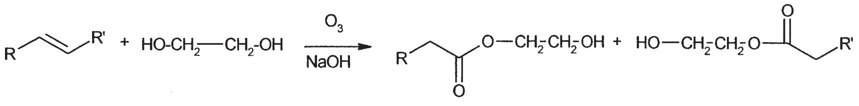


FIG. 1. Reduction of carbon-carbon double bonds in linoleic acid, used as a model compound, by alkaline catalytic ozonolysis of soybean oil with ethylene glycol. Error bars represent mean ± SD for *n* = 5 experimental runs.



SCHEME 1

NMR spectra were obtained on a 500 MHz model INOVA 500 instrument. Samples were dissolved in deuterated chloroform, and the ^{1}H NMR and ^{13}C NMR spectra were obtained at room temperature.

RESULTS AND DISCUSSION

Ozone is a very powerful oxidation agent and is well known to attack and cleave double bonds in alkenes. In addition to its high oxidation potential, ozone is convenient to use as an oxidizing agent since unreacted ozone simply decomposes back to oxygen and no special neutralization or separation is required at the end of the reaction. Furthermore, since ozone is being produced *in situ*, complex logistics in its transport, storage, and disposal are not required, as they are for many other oxidation agents. Linoleic acid was used as a model compound for our catalytic ozonolysis reaction. The disappearance of the carbon–carbon double bonds was determined by the iodine number test as shown in Figure 1. For each gram of oil all the double bonds were cleaved in 2 min under these conditions. It is well known that in the absence of reactive solvents, unstable 1,2,4-trioxolane and peroxide oligomers are formed by the Criegee mechanism and that these species eventually decompose to a mixture of aldehydes and carboxylic acids. Some products containing hydroxyl groups were also noted when ethylene glycol was present, even after repeated washing and separation to remove any traces of this alcohol from the oil. This is not surprising since alcohols (and protic solvents in general) are known to affect the rate of the reaction and to react with the ozonide intermediate (13). However, the course of the reaction is changed in the presence of an alkaline catalyst, which leads to an ester linkage between the decomposing ozonide intermediate and the alcohol (14). Accordingly, the ozonolysis reaction of alkene with excess ethylene glycol and an alkaline catalyst (e.g., NaOH) is expected to yield a mixture of polyols as shown in Scheme 1.

Similarly, when soybean oil is exposed to ozone in the presence of ethylene glycol and an alkaline catalyst, the cleavage of the carbon–carbon double bonds of the unsaturated FA yields a mixture of polyols. The composition of this polyols mixture is determined by the relative concentration of the unsaturated FA in the TG. Thus, oleic acid would be cleaved at the double bond at the ninth carbon leaving a (2-hydroxy)nonanoate residue on the TG and a (2-hydroxyethyl)nonanoate fragment (Fig. 2A).

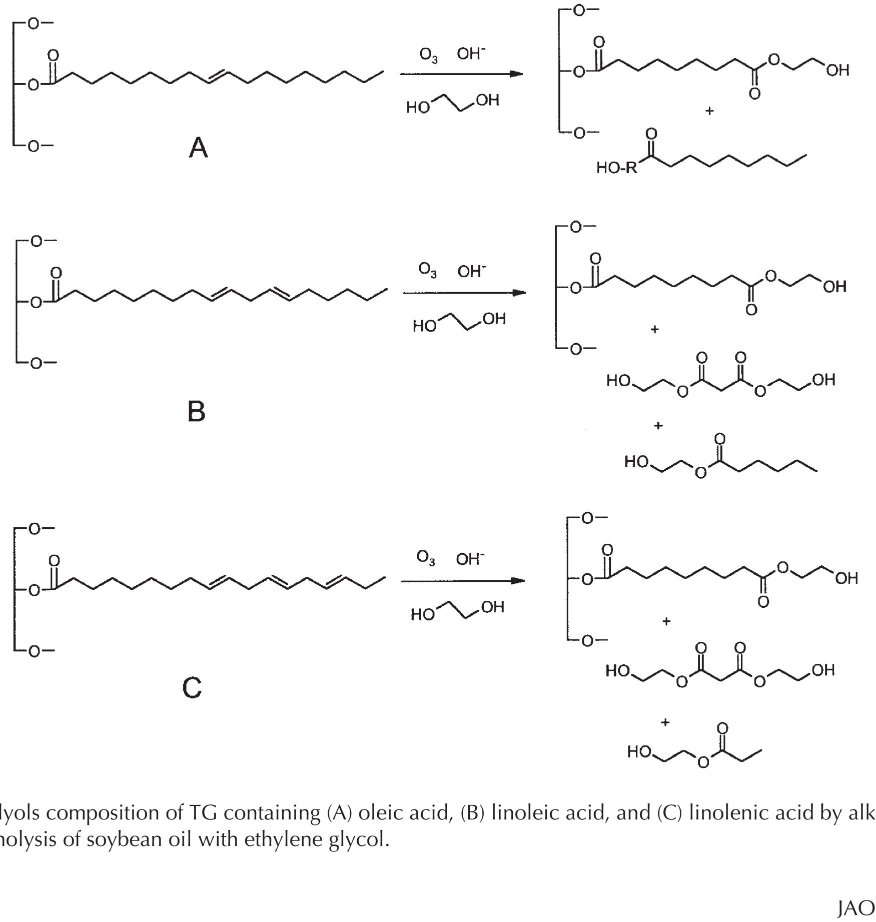


FIG. 2. Polyols composition of TG containing (A) oleic acid, (B) linoleic acid, and (C) linolenic acid by alkaline catalytic ozonolysis of soybean oil with ethylene glycol.

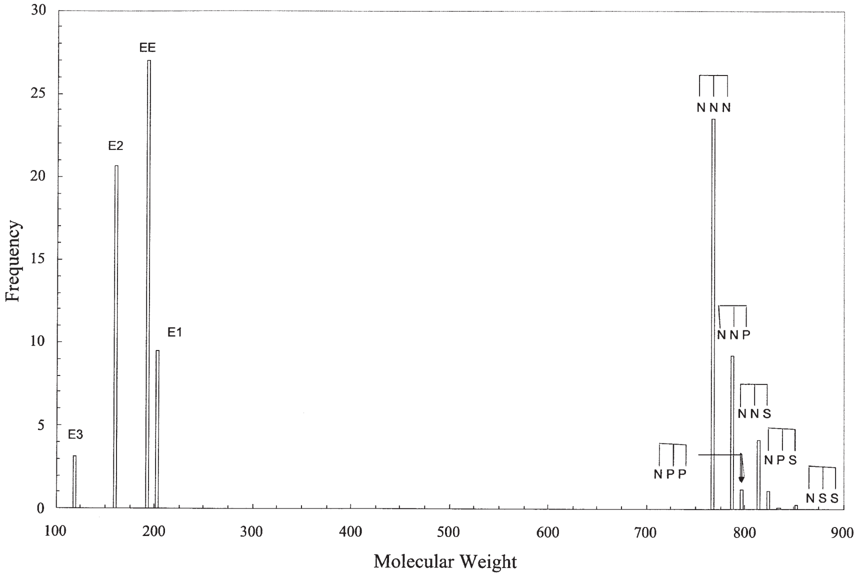


FIG. 3. Statistical distribution of soy polyols obtained by alkaline catalytic ozonolysis of soybean oil with ethylene glycol. N, nonanoate; P, palmitate; S, stearate.

Similarly, linoleic acid would be cleaved at the double bonds to yield a (2-hydroxy)nonanoate residue on the TG as well as (2-hydroxyethyl)hexanoate and bis(2-hydroxyethyl)malonate fragments (Fig. 2B). Linolenic acid, which contains unsaturations at the ninth, twelfth, and fifteenth positions would yield the same (2-hydroxy)nonanoate residue on the TG as well as (2-hydroxyethyl)propionoate and bis(2-hydroxyethyl)malonate fragments (Fig. 2C). Saturated FA (e.g., palmitic and stearic acids) are not cleaved by the ozone and remain intact. It is apparent from the structure of the unsaturated FA that, irrespective of the acid, cleavage occurs at the ninth carbon to yield (2-hydroxy)-nonanoate attached to the glycerol. Designating (2-hydroxy)nonanoate as N, palmitate as P, stearate as S, and arranging all possible permutations of these FA residues into TG leads to the following combinations: NNN, NNP, NNS, NPS, PPN, PPP, PPS, SSN, SSP, and SSS.

Additionally, the diol—bis(2-hydroxyethyl)malonate, designated here as EE—is obtained from hydrocarbon fragments between two double bonds as well as (2-hydroxyethyl)nonanoate, (2-hydroxyethyl)hexanoate, and (2-hydroxyethyl)propionoate fragments designated here as E1, E2, and E3, respectively.

The statistical distribution of these polyols can be determined by calculating the probability of finding these TG partitioned according to their relative abundance using a typical composition (15) of soybean oil (11 wt% palmitic acid, 4 wt% stearic acid, 23 wt% oleic acid, 51 wt% linoleic acid, and 7 wt% linolenic acid) as shown in Figure 3.

Several important points are apparent from this statistical analysis: (i) Overall, the polyol TG mixture is much more uniform than the original soybean oil TG composition since, after the ozonolysis, only three FA residues are present (instead of five) and about half of these TG are composed of NNN. (ii) About 24 wt% of the product mixture contains triols (NNN), 13 wt% contains diols (NNP and NNS), less than 3 wt% contains monofunctional alcohols (NPS, PPN, and SSN), and only a very small component (less than 0.2 wt%) of unreactive TG having no hydroxyl groups is present in the mixture. The very small quantity of unreactive components is very important as, on polymerization, it can migrate out the polyurethane or polyester and cause undesirable changes in properties. (iii) About half of the polyols product mixture is composed of TG and the other half is composed of the low M.W. diol (EE) and monofunctional alcohols (E1, E2, and E3). If needed, these low-M.W. species can be removed and separated from the polyol TG. However, in most cases this is not necessary as they will participate in the polymerization. It is also important to note that all these polyols are composed of primary hydroxyls, which are more desirable than secondary alcohols in the preparation of polyurethanes and polyesters.

The average functionality of the soy polyol mixture can be calculated from the statistical data using

$$f_{\mathrm{av}} = \Sigma n_i f_i / \Sigma n_i \quad [1]$$

where n_i is the number of moles of species containing functionality f_i. Accordingly, the maximum hydroxyl functionality is 1.9 per mole of soybean oil.

In practice, the hydroxyl functionality may be higher if the ozonolysis reaction is not terminated after all the double bonds are consumed and hydrocarbon chains are cleaved. Similarly, lower hydroxyl functionality than 1.9 is expected if the ozonolysis reaction is terminated before all the double bonds are consumed. Additionally, our calculation did not take into account complications such as the reaction of both hydroxyl groups of ethylene glycol. In this case, a high-M.W. product is expected if one ethylene glycol molecule reacts with two TG molecules. On

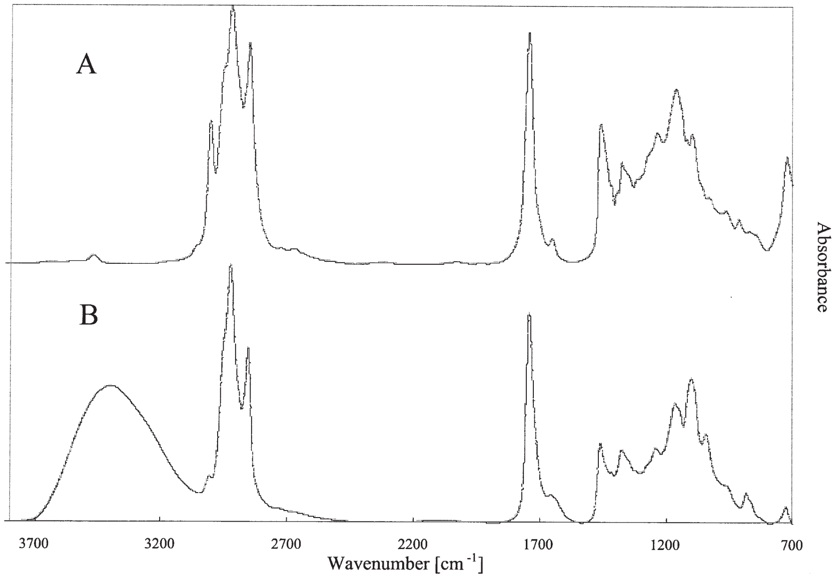


FIG. 4. FTIR spectra of (A) soybean oil and (B) soy polyol obtained by $CaCO_3$-catalyzed ozonolysis of soybean oil with ethylene glycol.

the other hand, intramolecular reaction, where ethylene glycol reacts with two FA in the same TG, will lead to cyclization and loss of hydroxyl functionality. Similar complications could arise when any of the hydroxyl-terminated fragments reacts with another TG instead of ethylene glycol. Most of these complications can be avoided, or at least greatly minimized, by using excess ethylene glycol in the reaction mixture.

The process conditions can further be adjusted to control the M.W. and the hydroxyl functionality of the product by using triols or other common low-M.W. polyols instead of ethylene glycol. Alternatively, the catalyzed ozonolysis reaction with polyethylene glycols of different M.W., instead of ethylene glycol, yields products containing different polyether chain lengths. Subsequent reaction of these polyols with isocyanates gives polyurethane foams with various degrees of flexibility, depending on the M.W. of the polyethers used in the ozonolysis reaction.

As expected, the soy polyol mixture is characterized by a broad hydroxyl stretching peak around 3500 cm^{-1}, the complete disappearance of the C=C band at 3005 cm^{-1}, and the C=C stretch at 1650 cm^{-1} (Fig. 4). This set of FTIR spectra further indicates that at the end of the ozonolysis reaction the carbonyl stretch at 1743 cm^{-1} became broader, suggesting the formation of new carbonyl compounds. A significant increase in the 1105 cm^{-1} band also was observed and was assigned to C–O stretching. No absorptions around 2900–2700 cm^{-1}, related to the C–H stretch adjacent to the carbonyl, were noted, indicating the absence of aldehyde groups.

In keeping the reaction time constant, the hydroxyl number was found to be directly proportional to the concentration of the NaOH and increased to 1.96 when 0.4 M NaOH was used. However, further attempts to use higher NaOH concentrations caused saponification of the TG ester linkages and the formation of free glycerol.

Possible saponification and the difficulty associated with removing traces of NaOH from the reaction mixture even after neutralization and repeated washing led us to examine alternative base catalysts. One class of potential catalysts we examined was amines (e.g., 4-DMAP, pyridine, triethylamine, tributylamine, dimethylamine, and hexamethylene diamine). The desired soy polyol products were obtained when any of these amines were used. As was the case with NaOH, the number of double bonds continuously decreased as a function of ozonation time, and the hydroxyl number simultaneously increased (Fig. 5). Unlike previous methods in the literature describing preparation of soy polyols, our one-step ozonolysis process appears to yield high hydroxyl numbers and primary alcohols in a simple, fast reaction. The rate of cleavage of the double bonds was independent of the amine catalyst and was directly proportional to the amount of ozone and the dispersion of the ozone bubbles in the reaction medium. Hydroxyl numbers were directly related to the type of amine used and its concentration. Although the reaction proceeded as anticipated, the color of the product was dark-yellow to brown depending on the type of amine that was used. Apparently, the observed discoloration was due to oxidation of the amine in the course of the reaction (16). Furthermore, strong bases like 4-DMAP led to saponification of the fatty esters in the soybean oil as was observed with NaOH.

Another class of potential catalysts that appeared most useful was inorganic alkaline oxides and carbonates (e.g., MgO and $CaCO_3$). These heterogeneous catalysts are effective and can simply be filtered out and removed from the reaction mixture with no need for neutralization. Also, they can be recycled and reused without any special treatment. To the best of our knowledge, only zeolites (17) have been claimed to be heterogeneous catalysts in ozonolysis reactions although these catalysts were

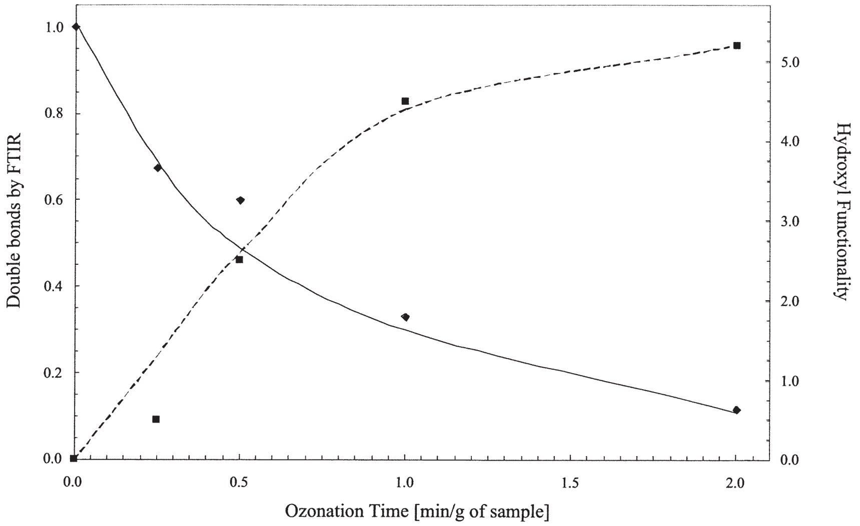


FIG. 5. Hydroxyl functionality (----) and double bonds (—) as a function of ozonolysis time in time of triethylamine-catalyzed ozonolysis of soybean oil and ethylene glycol.

used without additional hydroxyl compounds in the production of dicarboxylic acid from alkenes by ozonolysis. The progress of the reaction whereby double bonds were cleaved and hydroxyl groups were incorporated is clearly seen by FTIR (Fig. 6). In addition to convenient removal and recycling of this heterogeneous catalyst, the soy polyol product was an odorless, light-yellow oil suitable for production of polyurethanes and polyesters without further purification.

Further confirmation of the soy polyol structure was obtained from ^{13}C NMR spectra (Fig. 7). The characteristic double peak of double bonds at 130 ppm, related to the unsaturated FA in the soybean oil, does not appear in the soybean polyol

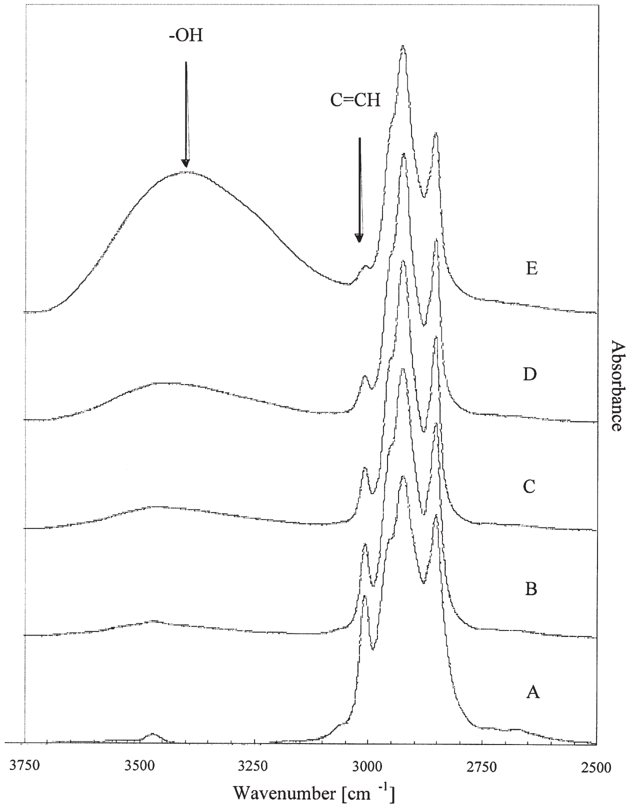


FIG. 6. Hydroxylation of soybean oil using $CaCO_3$ catalyst at different ozonation times. (A) t = 0; (B) t = 0.25; (C) t = 0.5; (D) t = 1.0; and (E) t = 2.0 min/g of soy oil. For each gram of oil all the double bonds were cleaved in 2 min.

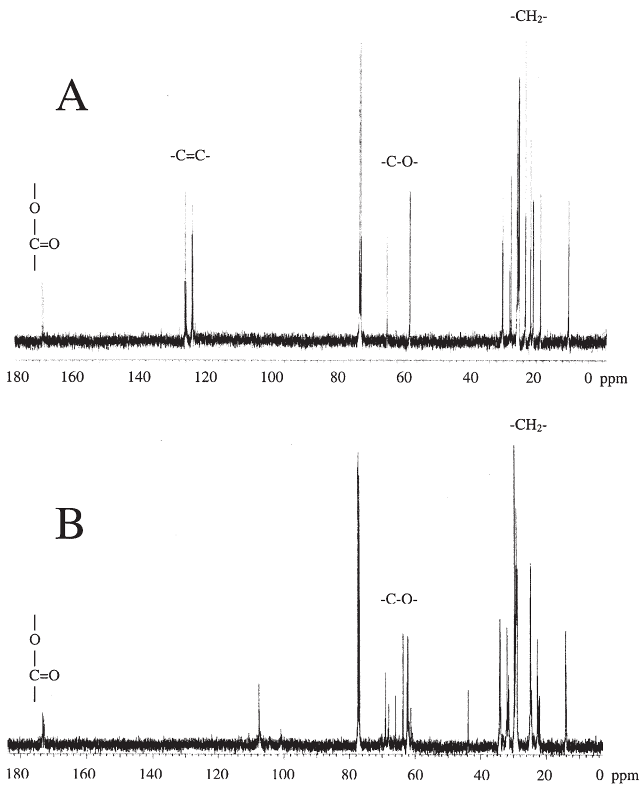


FIG. 7. ^{13}C NMR of soybean oil (A) and soy polyol obtained by $CaCO_3$-catalyzed ozonolysis of soybean oil with ethylene glycol (B).

spectrum, indicating complete cleavage of the double bonds. The carbonyl ester peaks (177 ppm) and the various methylene peaks (between 25 and 36 ppm) remained unchanged as did the glycerol carbons (64 and 69 ppm). Additionally, new resonance peaks appear at 66 ppm, which are related to ethylene oxide carbons, as well as peaks at 60 ppm, related to the new C–OH functional groups. It is apparent from the NMR data that the hydroxylation of soybean oil progressed as expected to yield the desired polyols.

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