

Chapter 6

Vegetable Oils-Based Polyols

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Introduction

Natural fats and oils normally consist of triglycerides of a mixture of fatty acids (FA). The FA part represents around 90% by weight and the glycerine part around 10% of the fat/oil molecule. The individual FA are characterized by the number of carbon atoms in the hydrocarbon chain, ranging generally from C8 (caprylic acid) to C22 (erucic acid) and additionally by the number of the double bonds in the chain. Typical FA compositions of selected natural oils are shown in [Table 6.1](#). One of the naturally occurring oils with an unusual chemical structure is castor oil, which typically comprises about 87% ricinoleic acid and has an average hydroxyl functionality of 2.7.

Polyurethanes are probably the most versatile group of polymers which can be used in the form of foams, cast resins, coatings, adhesives, and sealants. Polyols used in the polyurethane industry currently exceed 2.4 million tons/year in the U.S. (1). To use natural oils as raw materials for polyurethane production, multiple hydroxyl functionality is required. Castor oil has hydroxyl functionality naturally built in, thus it has received extensive exploration as polyurethane building blocks, such as casting resins, elastomers, urethane foams, and interpenetrating networks (2–8). Hydroxyl functionality can be introduced synthetically in other natural oils. This process involves a number of approaches and has been studied extensively by scientists around the world (2,9–47), but commercial production of oil-based polyols has been scarce. While the economics of the associated processes is certainly a large factor, properties of the product conforming to end-use play an important role.

Many problems remain to be solved. For example, commercial polyols for rigid urethane foams require an OH number of 450–500 mg KOH/g. Rigid foam production also requires the viscosity of the polyol component to <2,000 centipoises under ambient conditions for the purposes of easy processing and optimal product performance. Most oil-based polyols do not satisfy both requirements at the same time. Some of them have the right viscosity but have a low OH content; others have a high OH content but have turned to greases. Still others have lost their triglyceride linkages—an additional crosslinking naturally built into each oil molecule that enhances crosslinking and thus rigidity. Secondly, studies on the effect of

TABLE 6.1Typical Fatty Acid Compositions of Selected Plant Oils^a

Carbon atoms: Double bonds	8:0	10:0	12:0	14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:0	20:1	22:0	22:1	24:0	Iodine value range
Canola oil	—	—	—	0.1	4.0	0.3	1.8	60.9	21.0	8.8	0.7	1.0	0.3	0.7	0.2	100–115
Castor oil ^b	—	—	—	—	2.0	—	1.0	7.0	3.0	—	—	—	—	—	—	81–91
Coconut oil	7.1	6.0	47.1	18.5	9.1	—	2.8	6.8	1.9	0.1	0.1	—	—	—	—	7–12
Corn	—	—	—	0.1	10.9	0.2	2.0	25.4	59.6	1.2	0.4	—	0.1	—	—	118–128
Cottonseed oil	—	—	0.1	0.7	21.6	0.6	2.6	18.6	54.4	0.7	0.3	—	0.2	—	—	98–118
Linseed oil	—	—	—	—	6.0	—	4.0	22.0	16.0	52.0	0.5	—	—	—	—	>177
Olive oil	—	—	—	—	9.0	0.6	2.7	80.3	6.3	0.7	0.4	—	—	—	—	76–88
Palm oil	—	—	0.1	1.0	44.4	0.2	4.1	39.3	10.0	0.4	0.3	—	0.1	—	—	50–55
Palm kernel oil	3.3	3.4	48.2	16.2	8.4	—	2.5	15.3	2.3	—	0.1	0.1	—	—	—	14–19
Peanut oil	—	—	—	0.1	11.1	0.2	2.4	46.7	32.0	—	1.3	1.6	2.9	—	1.5	84–100
Rapeseed oil	—	—	—	0.1	3.8	0.3	1.2	18.5	14.5	11.0	0.7	6.6	0.5	41.1	1.0	100–115
Safflower oil	—	—	—	0.1	6.8	0.1	2.3	12.0	77.7	0.4	0.3	0.1	0.2	—	—	140–150
Safflower oil (high oleic)	—	—	—	0.1	3.6	0.1	5.2	81.5	7.3	0.1	0.4	0.2	1.2	—	0.3	82–92
Soybean oil	—	—	—	0.1	10.6	0.1	4.0	23.3	53.7	7.6	0.3	—	0.3	—	—	123–139
Sunflower oil	—	—	—	0.1	7.0	0.1	4.5	18.7	67.5	0.8	0.4	0.1	0.7	—	—	125–140
Sunflower oil (high oleic)	—	—	—	—	3.7	0.1	5.4	81.3	9.0	—	0.4	—	0.1	—	—	81–91

^aSome oil compositions may not add to 100% due to the presence of minor fatty acids. *Source:* Reference 48.^bContains 87% OH-bearing ricinoleic acid (C18:1).

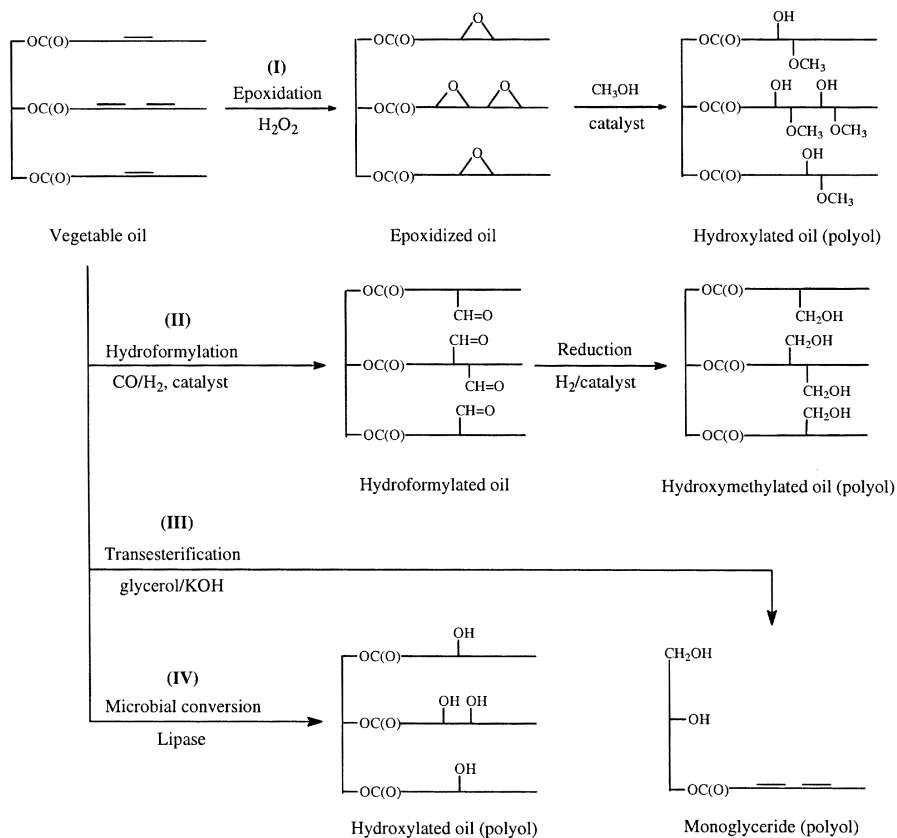
polyol structures derived from different vegetable oils on polyurethane properties have been largely lacking. However, such information is critical to the development of oil-based polyols, particularly regarding whether the methodologies employed for one oil can be adopted by another, or whether certain less available oils can be replaced by abundant oils in general polyurethane applications. On the other hand, oleochemical research peaked in the 1970s when a number of commercially feasible processes were identified (49).

Since then the associated technologies have advanced a great deal, thus prompting new opportunities for research and development of better processes. For example, most current commercial processes for the epoxidation of vegetable oils still rely on methodologies developed in the late 1940s, which do not lead to complete epoxidation, while a recent procedure using phase-transfer reagents was reported to result in quantitative epoxidation (50,51). As a second example, hydroformylation of olefins traditionally uses the vaporization technique for product-catalyst separation, which is not feasible for low-volatile substrates such as vegetable oils. Such a situation changed after Union Carbide developed the decantation process in the 1980s (52–59). Meanwhile, bulky phosphite-modified rhodium catalysts have been developed that show high reaction rates toward less reactive internal or branched olefins including fatty esters (5,60–72). Therefore, the development of a commercial process for the hydroformylation of fatty substances may have become imminent.

Preparation of Polyols from Vegetable Oils

The hydroxylation of vegetable oils can be achieved *via* four main approaches (Scheme 6.1). The first approach is the epoxidation or oxidation of the unsaturation followed by the ring-opening of the epoxides with proton donors (Scheme 6.1, Route I) (9,11–14,16–18,21,38,43,44,73–87). Secondary OH groups normally result from these procedures. A second approach of introducing hydroxyl functionality is the catalytic hydroformylation of the oils followed by reduction of the aldehyde oils (Scheme 6.1, Route II) (10,37,39,68,74,88–107), with primary OH groups being formed. Hydroxyl functionality can also be obtained by transesterification of oils with various types of polyols (Scheme 6.1, Route III) (84,108–116). Microbial conversion of oils to obtain polyhydroxy substances is also an emerging field (Scheme 6.1, Route IV) (117–121). A large number of publications and patents have appeared in the literature over the years.

The selection of vegetable oils depends mainly on the unsaturation level. While higher unsaturation of the oils leads to a higher OH content of the corresponding polyol, above a certain hydroxyl level the polyol suffers from a high viscosity. The theoretical OH numbers of vegetable polyols derived *via* the epoxidation route and the hydroformylation route are presented in Table 6.2. While coconut and palm kernel oils are of little value as polyol raw materials (i.e., OH number is too low), linseed oil has been reported to give a polyol behaving as a grease (10,96,97,122,123). Partial conversion of the double bonds in linseed oil



Scheme 6.1. Hydroxylation of vegetable oils.

may be optionally pursued to avoid high viscosity. The epoxidation of castor oil will be complicated because of the coexistence of oxirane and hydroxy groups (124). The hydroformylation of castor oil will produce a mixture of primary and secondary OH groups (2). Some oils appear to have similar composition such as soybean, corn, and sunflower oils. Triolein, trilinolein, and trilinolenin are included for comparison purposes.

Epoxidation and Alcoholysis

Each double bond in the oil molecule can be monohydroxylated or dihydroxylated depending on the use of oxidizing agents. The most studied monohydroxylation reaction involves a first epoxidation step using hydrogen peroxide, followed by a ring-opening step (Scheme 6.1, Route I) (9,11–14,16–18,21,32,38,43,44,73–87). Swern and Greenspan were among the first to epoxidize vegetable oils using peracetic acid (78,80,125–138). Most commercial processes available today producing

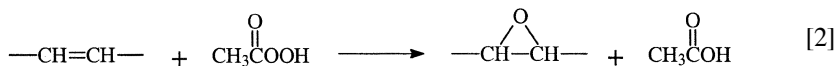
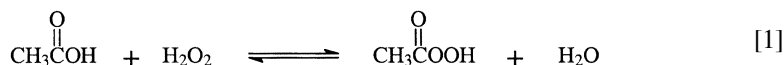
TABLE 6.2

Theoretical OH Number of Polyols from Plant Oils and Model Triglycerides

Oil type	Oil molecular weight	Total unsaturation ^a	OH number A ^b	OH number B ^c
Coconut oil	679	0.3	26	27
Palm kernel oil	707	0.6	46	46
Palm oil	848	1.8	109	113
Olive oil	878	2.9	158	166
Safflower oil (high oleic)	886	2.9	159	166
Sunflower oil (high oleic)	883	3.0	163	171
Triolein	885	3.0	163	171
Peanut oil	884	3.4	181	191
Rapeseed oil	953	3.9	190	201
Canola oil	882	3.9	206	219
Cottonseed oil	862	3.9	209	222
Corn	873	4.5	230	246
Soybean oil	874	4.6	236	253
Sunflower oil	877	4.7	239	256
Safflower oil	876	5.1	254	274
Trilinolein	879	6.0	288	314
Linseed oil	878	6.3	299	327
Castor oil ^d	928	3.1	307	322
Trilinolenin	873	9.0	387	435

^aNumber of double bonds per triglyceride based on Table 6.1.^bEpoxidation followed by methanolysis (addition of HO- and CH₃O- on each side of the double bond).^cHydroformylation followed by hydrogenation (addition of HOCH₂- and H- on each side of the double bond).^dNatural OH groups have been counted into the total OH number.

epoxidized oils are still based on the same principle. The process involves the *in situ* formation of peracid from glacial acetic or formic acid and H₂O₂ (Eq. 1), and oxidation of double bond by peracid to form epoxide regenerating acetic/formic acid at the same time (Eq. 2). H₂O₂ is consumed as a result:

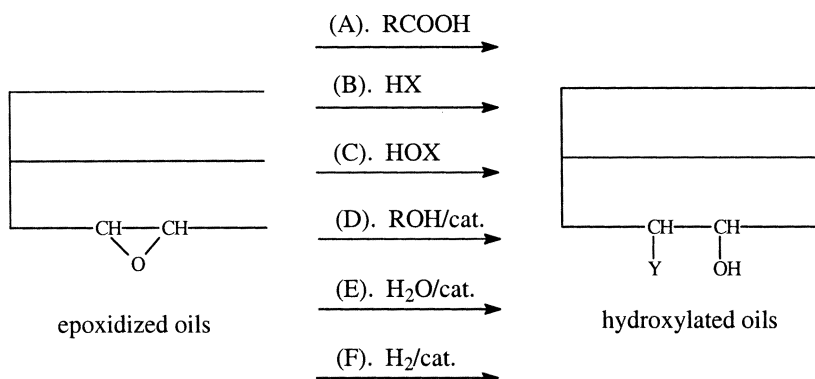


Quantitative conversions of double bond to epoxide are expected if the reaction time is long enough. However, side reactions become competitive after a certain period of time. Such side reactions involve the ring-opening of oxiranes by acetic acid or water (by-product), and further reaction of formed hydroxyl groups with oxiranes leading to polyether formation, which results in loss of epoxide content and/or rise in product viscosity (78,80,126). Therefore most epoxidation processes are stopped prematurely, resulting in typically 75–90% yield of epoxide.

While this level of epoxide content is sufficient for commercial products—whose uses are as plasticizers for polyvinyl chloride—the preparation of polyols desires a maximized epoxidation. A number of new procedures have developed in recent years toward expediting the epoxidation process by using catalysts, applying pressure, using phase-transfer reagents (PTR), or using other oxidizing agents (50,51,79,124, 139–158). Among others, catalysts used include ion-exchange resins, sulfuric acid, molybdenum or tungsten oxide, and methyltrioxorhenium/pyridine. Quaternary ammonium salts of tetrakis(diperoxotungsto)phosphates(3-) are PTR reportedly efficient for the epoxidation of vegetable oils (51). The use of these reagents in conjunction with medium-strength hydrogen peroxide (30%) as the primary oxidant in an aqueous/organic biphasic system provides an efficient, versatile, and synthetically valuable catalytic method for olefin epoxidation. By this method, a variety of water-insoluble inactivated alkenes, internal or terminal, acyclic or cyclic, isolated or carrying diversified functionalities, were epoxidized in high yields under mild conditions and after relatively short reaction times. The process normally requires no solvents, and the use of medium-strength hydrogen peroxide also lessens safety concerns associated with the explosion hazard of various peroxides. Crivello has recently demonstrated that a series of vegetable oils were epoxidized in high yield by using either a PTR or a sulfonated ion-exchange resin (50,158–162). Methyltrioxorhenium/pyridine has also recently been reported to be a very efficient catalyst for the epoxidation of soybean oil (139), although the process suffers from the toxicity of pyridine.

The dihydroxylation of fatty substances has been studied by a number of workers (124,126,130,153,163–167). Osmium, selenium, titanium, and other catalysts have been reported. Although they are efficient for discrete FA derivatives, some of the procedures involve strongly basic conditions that would hydrolyze the triglyceride and thus are generally not applicable to vegetable oils. For example, according to the authors' observation, $\text{H}_2\text{O}_2/\text{OsO}_4$ gives a grease for the oxidation of soybean oil with a low OH content, while SeO_2 is believed to form a complicated mixture of products if applied to neat linoleic acid. The toxicity of osmium excludes its use in a commercial process, even in catalytic amounts. Therefore dihydroxylation procedures have been pursued scarcely.

Although the very reactive oxirane groups in the epoxidized oil molecule enable a number of ring-opening reactions to convert the epoxidized oils to hydroxylated oils, such as carboxylation, alcoholysis, hydrolysis, or hydrogenation ([Scheme 6.2](#)) (9,11–14,16–18,21,33,34,37,44,47,73–87), not all are applicable to the preparation of polyols. According to the authors' experience with the soybean oil system, carboxylation (Route A) leads to a number of complications (oligomerization, cyclization and esterification) resulting in a high viscosity and a low OH content of the polyol. Hydrohalogenation or hydrohyperhalogenation (Routes B and C) gives rise to very good conversion of the material, but the products are highly viscous greases under ambient conditions. Hydrogenation of ESBO (Route F) gives a semi-solid with a melting range of 40–60°C. Hydrolysis (Route E) produces a viscous product having half of the expected OH content owing to the presence of a number of side reactions.



Scheme 6.2. Hydroxylation reactions of epoxidized oil, where $\text{Y} = -\text{OC}(\text{O})\text{R}$ for (A); X for (B); $-\text{OX}$ for (C); $-\text{OR}$ for (D); $-\text{OH}$ for (E) and $-\text{H}$ for (F), and $\text{X} = \text{Cl}$ or Br .

Alcoholysis (Route D) is the only workable approach to prepare oil-based polyols. Epoxidized soybean oil can be alcoholized almost quantitatively in the presence of an acid catalyst, and the polyols produced as such possess low viscosities and nearly theoretical OH contents (18,33,34, 37,44,47).

A series of vegetable oil-based polyols have been prepared *via* a two-step process starting from the vegetable oils, i.e., epoxidation by *m*-chloroperoxybenzoic acid, or by hydrogen peroxide catalyzed by a PTR or a sulfonated resin (50,158), followed by methanolysis (18,38). Some of the polyols prepared from *m*-chloroperoxybenzoic acid suffered from incomplete epoxidation as evidenced by Fourier transform infrared (FT-IR) and nuclear magnetic resonance (NMR) results of epoxidized samples, indicating that *m*-chloroperoxybenzoic acid is not an efficient peroxidant, while the PTR or resin-catalyzed epoxidation proceeded smoothly. The epoxidation products generally require purification before the hydroxylation step.

FT-IR has proved to be an effective tool for the analysis of epoxidized oils. The double bond in the oil molecule shows a strong absorbance at 3011 cm^{-1} (C-H stretch), while the oxirane groups give a weak but distinctive twin band at 823 cm^{-1} (deformation) and 845 cm^{-1} (asymmetric stretch), and a shoulder band at 1263 cm^{-1} (symmetric stretch). The intensity change in these bands during epoxidation is sharp enough to monitor the progress, although ^1H -NMR can be equally effective (5.4 ppm for vinylenic protons, and 2.9/3.1 ppm for epoxy methine protons). However, FT-IR is only qualitative for the measurement of polyol OH content since the OH band at 3440 cm^{-1} is very broad and is highly sensitive to impurities containing OH groups.

Catalytic Hydroformylation and Reductive Hydrogenation

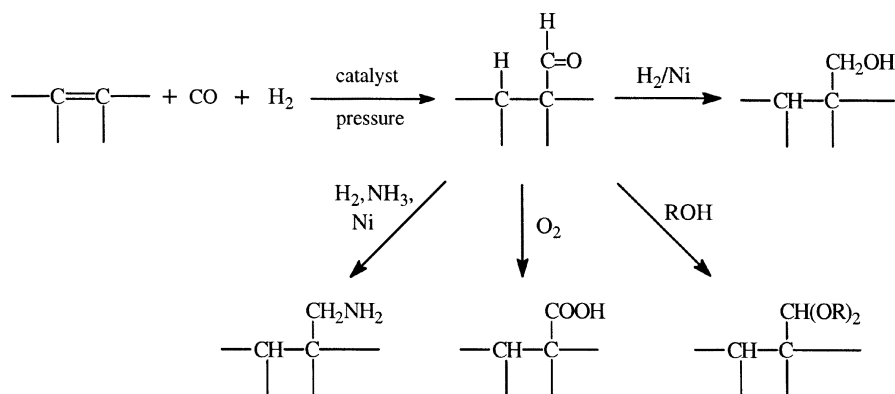
Hydroformylation of olefins has become a very mature and important industrial process since its discovery in 1938 (168). Olefins can be hydroformylated by treat-

ment with *syngas* and a catalyst, yielding aldehydes that contain an additional carbon atom. This reaction is a mild and clean procedure for functionalizing unsaturated compounds and is compatible with many other functional groups, such as esters, carboxyls, amides, ketones and even hydroxyls. The atom economy of the reaction is 100%, i.e., all atoms of the reactants end up in the product (169), which results in a minimum of chemical waste discharge (Scheme 6.3). The aldehydes produced form the base for many subsequent transformations leading to alcohols (reduction), amines (reductive amination), carboxylic acids (oxidation), acetals, etc. Significant advancements in hydroformylation have been made over the last few decades. Aspects involve: (i) catalyst/ligand modification; (ii) product/catalyst separation; (iii) process modification including heterogeneous and biphasic catalysis, low pressure hydroformylation, and the addition of decanting process and catalyst recycling. Over the years, people all round the world have showed tremendous interest in the oxo processes. Hundreds of scientific publications and patents appear each year.

The three main types of catalyst used commercially are (i) simple cobalt carbonyl complexes, (ii) cobalt carbonyl complexes modified by tertiary phosphine/phosphite ligands, and (iii) tertiary phosphine/phosphite rhodium carbonyl species. Although most industrial processes still use cobalt, more than 90% of the oxo plants built since 1977 use rhodium-based catalysts and low-pressure oxo (LP OXO) technology developed by Union Carbide.

Other metals such as iridium, platinum, ruthenium, manganese, iron, copper, silver, bimetallic species and metal clusters are also known catalysts. Polymer-supported and other heterogeneous catalysts have also been developed. These catalyst systems are all in the research stage, and still far from commercialization.

Cobalt has been the conventional catalyst for hydroformylation. However, cobalt is not a very active catalyst. It requires high temperatures and high pressures [typically 140–180°C at 250–350 bars, see Table 6.3 (170)]. High temperatures



Scheme 6.3. Hydroformylation of olefins.

TABLE 6.3Comparison of Olefin Hydroformylation Catalysts^a

	Unmodified cobalt	Phosphine-modified cobalt	Phosphine-modified rhodium
Temperature (°C)	140–180	160–200	80–120
Pressure (bar)	250–350	50–100	15–25
Catalyst concentration (% metal/alkene)	0.1–1.0	0.5–1.0	10 ⁻² –10 ⁻³
Linear/branched ratio	3–4:1	6–8:1	10–14:1
Aldehydes (%)	80	none	96
Alcohols (%)	10	80	none
Alkanes (%)	1	15	2
Other products (%)	9	5	2

^aUsing α -olefin as feedstock (170).

degrade selectivities since side reactions have become a problem. Such side reactions include hydrogenation of aldehydes to alcohols and of olefin to alkanes, aldol additions of aldehydes to give dimer aldehydes and ester triols, hydroformylation of aldehydes to formate esters, and reaction of aldehydes with byproduct alcohols to give acetals. Meanwhile, high-pressure operations require expensive construction of process plants. Phosphine or phosphite modification of the cobalt catalyst leads to reduction of the process pressure (down to 50–100 bars). However, there is a significant amount of hydrogenation by-products being produced (15%) along with the rapid reduction of the aldehyde to alcohol (80%) during hydroformylation (although this anomaly may be advantageous to this project since the reduction step is eliminated). On the other hand, the rhodium catalyst requires only very low process pressures (15–25 bars) and also lower temperatures (80–120°C) resulting in nearly quantitative conversion (96%) of olefin to aldehyde.

The discovery in the early 1980s by Bryant (Union Carbide, Charleston, WV) and van Leeuwen (Shell Lab, Amsterdam, The Netherlands) of bulky phosphite ligand modified catalysts showing high reaction rate for otherwise unreactive (internal and branched) olefins is a major breakthrough in hydroformylation catalysis (5,60–72). Owing to their high reactivity, these bulky phosphite-modified catalysts have offered new possibilities for the development of a commercial process for the hydroformylation of FA and derivatives including vegetable oils. Significant progress has also been made in the area of product/catalyst separation for the hydroformylation of higher olefins. Hydroformylation as a homogenous process has traditionally used the vaporization technique in commercial processes, but they are limited to those with volatile products, i.e., to the hydroformylation of lower olefins. The recent introduction by Union Carbide of a single-phase oxo process by using organic media-soluble ionic triarylphosphines or phosphites ligands and of product/catalyst separation by decantation has revolutionized the hydroformylation technology. This process permits the hydroformylation of higher molecular weight

and non-volatile olefins such as fatty substances. The single-phase rhodium-ionic phosphine catalysts have the reactivity typical of conventional homogenous hydroformylation catalysts. However, they can be easily induced to separate into non-polar (product) and polar (catalyst) phases, thereby providing an effective means for product separation and catalyst recovery (52,54–57,59,171–182).

A variation of the Union Carbide single-phase oxo process has been under the extensive investigation of Fell *et al.* (98,183,184). This process allows the hydroformylation of polyunsaturated substances such as FA esters in a polar solvent (methanol) in the presence of a rhodium-ionic phosphine catalyst. After the reaction, the methanol is distilled off; the catalyst system becomes insoluble and can be separated from the reaction product by filtration or by extraction with water. The aqueous catalyst solution is evaporated to dryness and the catalyst system dissolved in methanol for a new reaction. However, the process is limited to polar media-soluble fatty substances applying a fairly high pressure (e.g., 70–200 bars). Heterogeneous systems using supported rhodium catalysts for the hydroformylation of fatty substances were also studied and it was concluded that these systems are limited to the hydroformylation of mono- and diunsaturated FA (e.g., oleates and linoleates) and are ineffective with triunsaturates (e.g., linolenates).

USDA's research activities on the hydroformylation of fatty substances were during the 1970s (2,10,88–90,92–96,100–103,106,107,122,185–190). A number of vegetable oils were investigated including soybean, linseed, castor, safflower oils, and their derivatives. While the hydroformylated fatty products were suggested for uses as plasticizers for polyvinyl chloride and as coatings, rigid urethane foams prepared from hydroformylated polyols were also reported. The best catalyst systems used at the time were triphenylphosphine- or triphenylphosphite-modified rhodium catalysts normally requiring at least 2,000 psig of *syngas* pressure, although a much lower pressure (200 psig) is needed for methyl oleate. Although monounsaturated fatty substances can be readily hydroformylated under mild conditions, di- and triunsaturated FA derivatives were found to require higher pressures owing to the presence of π -allylic intermediates, which slowly undergo hydroformylation. The isomerization of double bonds from *cis* to *trans* and that from nonconjugated to conjugated have been noted by several workers, and it has been understood that these phenomena are responsible for the slowdown in hydroformylation rate (61,62,64,69,71,72,95,103,191).

Although much attention has been paid to the regioselectivity issue on the hydroformylation of various olefins, this information may have limited value as far as the preparation of oil-based polyol is concerned. The hydroxymethyl groups will be located internally in the FA chains, the positions of which differ by only one carbon atom. Since each triglyceride molecule contains many isomers randomly distributed in the three fatty chains, it would be impossible to identify the effect of isomerization on the properties of the crosslinked polyurethane materials, even if a model triglyceride is used. The same is true of the polyols prepared from the epoxidation approach, where the secondary OH groups may be placed in either side of the double bond.

A recent study has proved that the bulky phosphite-modified rhodium catalyst is several times more active than triphenylphosphine-modified catalyst (64). Vegetable oil-based polyols have been prepared using Rh/C (5% rhodium on carbon) or $\text{Rh}(\text{CO})_2(\text{acac})$ as catalyst precursors. Polyols of this type are expected to have an OH number and a viscosity in the same range of polyols prepared *via* the epoxidation route (see Table 6.2). When tris(2,4-di-*t*-butylphenyl) phosphite is used as ligand using an olefin/Rh molar ratio of 800–1,000, P/Rh ratio of 25, and a total pressure of 500–1,000 psig, the reaction is completed within a few hours at 100°C, as is evidenced from the soybean oil system.

Bidentate phosphite ligands (192–196) and ionic phosphite ligands (54,57, 59,178) have also been examined. Whatever the case, the spent rhodium must be fully recovered in order to be commercially practical. The reductive hydrogenation of aldehyde oils has been conducted at 1,000 psig of hydrogen pressure using Raney nickel as the catalyst as demonstrated by many workers (2,186,197). Sodium borohydride can alternatively be used, but reaction conditions have to be controlled carefully in order not to hydrolyze the triglyceride linkages. Kinetic study has been carried out to characterize the catalyst reactivity. These aspects include varying the temperature, H_2 and CO pressures, catalyst concentration, and ligand-to-metal ratio. Since the kinetics for the hydroformylation of vegetable oils is very complicated owing to the presence of a mixture of olefins (mono-, di-, and trienes), triolein, trilinolein, and trilinolenin have been used for the kinetic study (104,105).

For the analysis of hydroformylated products, FT-IR is used. The aldehyde groups give a strong band at 1728 cm^{-1} (C=O stretch, shoulder to triglyceride carbonyl at 1744 cm^{-1}) and a medium broad band at 2701 cm^{-1} (C-H stretch/bend). The intensity change in these bands can be used to monitor the progress of hydroformylation. NMR can also be optionally employed. Vinylene protons are at *ca.* 5.4 ppm and the aldehyde proton appears further downfield (*ca.* 10 ppm). The carbonyl content of the aldehyde oil can also be analyzed according to a titrimetric procedure (198).

Transesterification

The transesterification of vegetable oils with glycerine leads to the formation of mono- and diglycerides. A polyol is formed in a single-step transformation and thus the process is of interest from the commercial point of view (84,108–116,199). Other polyhydroxy compounds can be used in the place of glycerine such as trimethylolpropane, pentaerythritol, among others. However, this process leads to no hydroxylation of the double bonds in the FA chain. The FA chains are simply dangling, and thus may not contribute to mechanical strength of the end products. These chains may actually lower the mechanical properties of the products due to their plasticizing effect.

Microbial Conversion

The microbial hydroxylation of oils is an emerging field (117–121,200). Polyols are produced in a single step under mild conditions using an enzyme as the catalyst

and oxygen from the air and/or water as the reagents. In contrast to the chemical processes mentioned above (i.e., epoxidation, and hydroformylation) where the hydroxy groups are attached to the double bond positions in the FA chain, the hydroxyls generated enzymatically are normally alpha to the double bonds in the chain. Although these processes appear attractive environmentally, they are still far from the commercial stage mainly due to the overwhelming cost of the catalysts.

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