

Production of Polyols from Canola Oil and their Chemical Identification and Physical Properties

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Received: 8 February 2006 / Accepted: 3 November 2006 / Published online: 14 December 2006
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Abstract The feasibility of a method based on ozonolysis and hydrogenation reactions for the production of polyols from unsaturated canola oil has been demonstrated. Polyol products with primary alcohol functional groups at position nine of each fatty acid ester in the original triacylglycerol have been produced from canola oil. Short straight-chain alcohols were also produced and were removed by wiped-blade molecular distillation. The pure components of the polyol, i.e. mono-ol, diol and triol were separated by flash chromatography, and identified by Fourier-transform infrared (FTIR), ^1H -nuclear magnetic resonance (NMR), ^{13}C -NMR as well as mass spectrometry. Polyol identification was facilitated by the use of a simple high-performance liquid chromatography (HPLC) method to determine the composition of the polyol mixture, which can be exploited as a quality-control mechanism in designing novel polyol feedstocks. Basic correlations were established between the molecular diversity of the polyols and their physico-chemical properties, such as hydroxyl number, acidity number, and viscosity. It has been found that the produced polyols are suitable for processing methods employing polyols for the production of polyurethanes and can be manipulated to create polyurethanes with desirable properties.

Keywords Canola oil · Hydroxylated triglycerides · Polyol production from canola oil · Triol

Introduction

Polymeric materials, such as polyurethanes (PUs) are traditionally derived from petrochemical polyols [1], but as oil reserves are depleting and prices continue to rise, the development of alternatives is becoming necessary [2–4]. Worldwide economic and scientific interest in vegetable oils as an inexpensive, readily available renewable resource is growing and has already been the subject of significant attention [5]. Native North American vegetable oils are comprised mainly of triacylglycerols (TAGs) containing predominantly unsaturated fatty acids, which are chemically relatively unreactive. In order to produce reactive materials which then can be utilized in producing valuable polymeric materials, functional groups such as hydroxyl, epoxy, or carboxyl groups have to be introduced at the positions of double bonds of the unsaturated TAGs [6–9].

As a low-cost and easily produced reagent, ozone is widely used to oxidatively cleave the double bond of an alkene [10]. In the 1960s and 1970s, Pryde's group [11–13] successfully applied ozonolysis on methyl oleate to produce alcohol and aldehyde. Employing similar procedure, soybean oil was also used as feedstock to make aldehyde oils [14–16]. More recently, Petrovic et al. [6] used ozonolysis followed by reduction to make a triol product from triolein, soybean oil and canola oil.

Canola vegetable oil is a good candidate for the production of polyol using ozonolysis and hydrogenation reactions. It contains more than 90% of unsaturated

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fatty acids, including oleic acid, linoleic acid, and linolenic acid [17], which all have a double bond at carbon nine that could be easily cleaved and the cleavage products hydrogenated to provide terminal functional groups. The probability of forming a single alcohol group (which is a chain terminator) on a TAG would be in this case very low. Triolein has been used as an example, the mechanism leading to the production of polyols from unsaturated TAG is illustrated by the reaction shown in Fig. 1.

In this study, ozonolysis and hydrogenation technology was used to produce polyol from canola oil. The identification of the polyol and of valuable side-products are presented. The physical properties of the polyol are also reported.

Experimental Procedures

Materials

The canola vegetable oil used in this study was a 100% Pure Canola supplied by Canbra Foods Limited, Lethbridge, AB, Canada. Raney nickel 2800 (slurry in water) catalyst was obtained from Sigma-Aldrich Co., USA. Celite, dichloromethane (HPLC grade), heptane (HPLC grade), 2-propanol (isopropanol, HPLC grade), ethyl acetate and hexane were obtained from Fisher Scientific, USA. Tetrahydrofuran (THF) was obtained from Caledon Laboratories Limited, ON, Canada. Silica

gel (230–400 mesh) was obtained from Rose Scientific Ltd, AB, Canada. All chemicals were reagent grade or better.

Ozonolysis

An ozonolysis batch consisted of about 100 g of canola oil and 400 g of deionized water. The mixture was poured into a specially designed reactor (Fig. 2), powered with a direct-current permanent-magnet 1 HP motor from Leeson Electric-Corporation, USA. Ozone was produced in an ozone generator (Azcozon Model RMV16-16 from Azco Industries Ltd, Canada) with oxygen or air as the feed gas. The reaction was performed at 0 °C, at 5 L/min air or oxygen flow rate and 500 rpm agitation rate for 8 h. The concentration of ozone was 62 g/m³ when oxygen is used and 29 g/m³ when air is used. After 8 h, the ozone generator was stopped and the reaction vessel was purged with N₂ for 10 min to remove the unreacted ozone in the vessel. The product of ozonolysis was dissolved in 400 mL of THF and transferred to a separatory funnel where the organic phase was separated from the aqueous phase and collected for hydrogenation.

Hydrogenation

Fifteen grams of Raney nickel catalyst (RA-Ni) (slurry in water) was added to the ozonolysis product in a hydrogenation vessel (2 L, Parr Instrument Co.,

Fig. 1 Mechanisms leading to the production of polyol from unsaturated TAG. Example of triolein

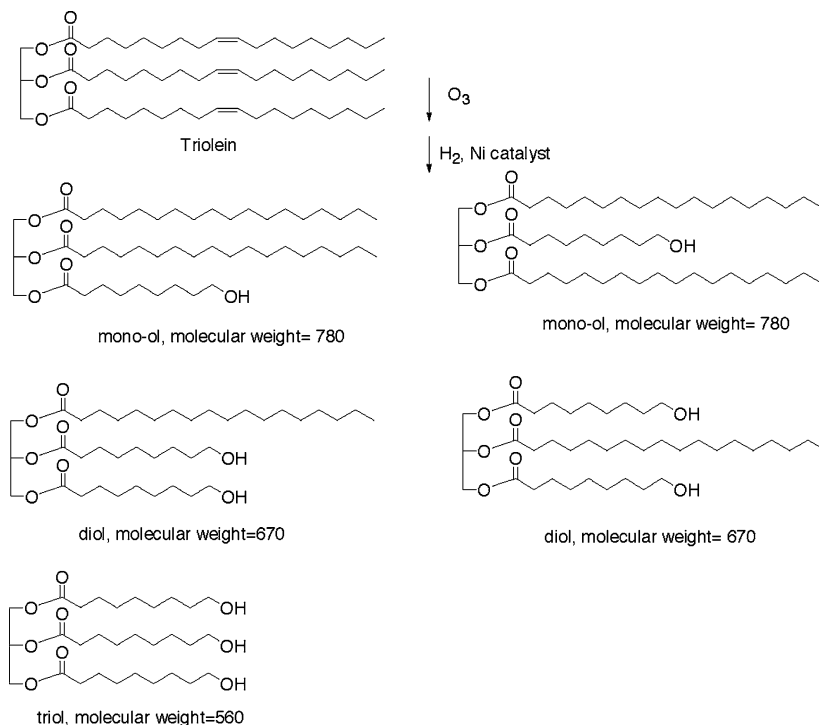
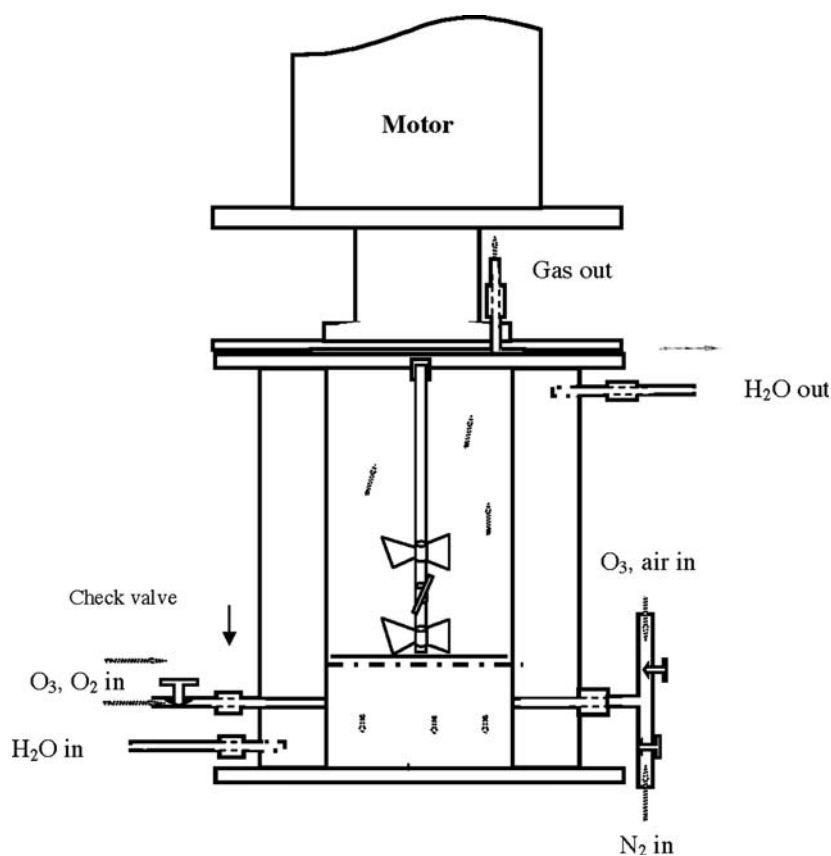


Fig. 2 Schematic of the ozonolysis reaction vessel



USA) fitted with a magnetic drive. The reaction vessel was charged with hydrogen gas to 350 psi at room temperature. The temperature was then increased to 130 °C. After 8 h, the temperature was reduced to room temperature. The reaction vessel was finally purged with nitrogen gas to remove unreacted hydrogen gas. The resulting mixture was filtered over Celite and the aqueous layer was removed. The solvent was then removed from the organic layer by rotary evaporation and the final product was kept for distillation.

The presence of nonanal, easily tested by gas chromatography (GC), was used as an indicator of the completion of hydrogenation.

Wiped-Blade Molecular Distillation

The unit (Model VKL 70/ICL-04, from Incon Processing, IL, USA) was set up at a jacket temperature of 115 °C and condenser temperature of 30 °C. The pressure of the distillation system was reduced to 20 mtorr and the final hydrogenation product added into the distillation system through an addition funnel at a rate of 1 mL/min. The polyol was collected in the residue part because of its high boiling point, and the

short-chain molecules cleaved from the fatty acid chain were distilled and condensed in the distillate part.

The polyol obtained when using oxygen is referred to as Canola-Oxygen Polyol, and the polyol obtained when using air is referred to as Canola-Air Polyol.

High-Performance Liquid-Chromatography System

The high-performance liquid-chromatography (HPLC) analysis protocol used was a modification of the procedure developed by Elfman-Borjesson and Harrod [18] for the analysis of lipid derivatives. The HPLC system consisted of a dual Milton Roy pump with a 20 μ L auto-injector. The column was packed with Betasil Diol-100 (5 μ m particle size) 250 mm \times 4 mm produced by Thermo Hypersi-Keytone and maintained at 50 °C with a Biorad column heater. The detector was an Alltech ELSD 2000 evaporative light scattering system maintained at 100 °C with a gain setting of 10 (on the 12 unit scale) and a nitrogen pressure of 2 bar. Two solvents (*A* and *B*) were connected to the pump as the mobile phase. *A* was 100% heptane and *B* was 50% heptane with 50% isopropyl alcohol (IPA). A run consisted of a linear gradient of 100% *A* to 83% *A* and

17% *B* in 30 min; then back to 100% *A* in 1 min at a flow rate of 3 mL/min.

Flash Chromatography

A total of 4.3 g of Canola-Oxygen Polyol components were separated in a column of dimensions 3 cm × 30 cm packed with silica gel (230–400 mesh). The column was eluted with gradient flow phase composed of hexane and ethyl acetate. The ratio (v/v) of hexane to ethyl acetate was started at 50:1, then gradually decreased to 20:1, 17:1, 10:1, 8:1, 5:1, 3:1, 2:1, 1:1, followed by 1:2, 1:3, 1:4. Finally pure ethyl acetate was used and the fractions were collected in 30 mL test tubes. Thin-layer chromatography (TLC) was run on each fraction using hexane and ethyl acetate as the developing system with ratios (v/v) of hexane and ethyl acetate of 3:1, 2:1, and 1:1. The final collected pure fractions, i.e. saturated TAGs (ratio of flow phase of 20:1), mono-ol (ratio of flow phase of 8:1), diol (ratio of flow phase of 2:1) and triol (ratio of flow phase of 1:4), were analyzed by HPLC, Fourier-transform infrared (FTIR), ¹H-NMR, ¹³C-NMR and mass spectrometry.

Gas Chromatography System

Varian 3500 capillary GC equipped with a flame ionization detector (GC-FID), Varian 8200 auto sampler and a BP20025 column (30 m × 0.25 mm i.d., 0.25 μm) was used to identify and quantify the short-chain compounds present as by-products of the hydrogenation reaction. The injector and the detector temperature were fixed at 250 °C. The temperature of the column initially set at 50 °C was increased to 250 °C in two successive steps: from 50 to 90 °C at a rate of 25 °C/min and from 90 to 250 °C at a rate of 10 °C/min.

FTIR, ¹H-NMR and Mass Spectrometry

FTIR spectra were measured with a Mattson Galaxy Series FT-IR 3000 spectrophotometer. ¹H-NMR and ¹³C-NMR were recorded at 500 or 400 MHz Varian spectrometers (Varian, Inc., CA, USA) with CDCl₃ as a solvent. Mass spectra were acquired on a Biosystem Mariner high-resolution electrospray positive-ion-mode spectrometer (PerSeptive Biosystems, Inc., MA, USA).

Saturated TAG

¹H-NMR (CDCl₃ 500 MHz): δ 5.26 (m, 1H, CHOCOR), 4.29 (dd, *J* = 4.0 Hz, 12.0 Hz, 2H, CH₂OCOR),

4.14 (dd, *J* = 5.5, 11.5 Hz, 2H, CH₂OCOR), 2.30 (t, *J* = 7.5 Hz, 6H, CH₂CO), 1.60 (m, 6H, CH₂CH₂CO) 1.20 (m, 84, CH₂), 0.88 (t, *J* = 7.0 Hz, 9H, CH₃). ¹³C-NMR (CDCl₃ 125 MHz): δ 173.3 (COR, *sn*-1, 3), 172.92 (COR, *sn*-2), 172.86 (COR, *sn*-2), 68.94 (CHOCOR), 62.16 (CH₂OCOR), 34.28, 34.12, 31.98, 29.76, 29.72, 29.68, 29.54, 29.42, 29.35, 29.33, 29.18, 29.15, 24.97, 24.93, 22.74, 14.58 (CH₃).

Mono-ol

¹H-NMR (CDCl₃ 500 MHz): δ 5.26 (m, 1H, CHOCOR), 4.29 (dd, *J* = 4.5, 12.0 Hz, 2H, CH₂OCOR), 4.14 (dd, *J* = 6.0, 11.5 Hz, 2H, CH₂OCOR), 3.62 (t, *J* = 6.5 Hz, 2H, CH₂OH), 2.30 (t, *J* = 7.5 Hz, 6H, CH₂CO), 1.60 (m, 8H, CH₂CH₂CO and CH₂CH₂OH), 1.20 (m, 64H, CH₂), 0.88 (t, *J* = 6.5 Hz, 6H, CH₃). ¹³C-NMR (CDCl₃ 125 MHz): δ 173.34 (COR, *sn*-1, 3), 173.32 (COR, *sn*-1, 3), 173.26 (COR, *sn*-1, 3), 172.91 (COR, *sn*-2), 172.84 (COR, *sn*-2), 68.94 (CHOCOR), 68.93 (CHOCOR), 62.98 (CH₂OCOR), 62.15 (CH₂OH), 62.11 (CH₂OH), 34.25, 34.20, 34.09, 34.03, 32.77, 32.76, 31.96, 29.73, 29.71, 29.69, 29.68, 29.65, 29.53, 29.51, 29.39, 29.33, 29.30, 29.23, 29.21, 29.20, 29.19, 29.15, 29.11, 29.01, 28.98, 25.70, 25.68, 24.94, 24.90, 24.86, 24.83, 22.72, 14.13 (CH₃). CI-MS: *m/z* 803.7 ([M+Na]⁺).

Diol

¹H-NMR (CDCl₃ 400 MHz): δ 5.26 (m, 1H, CHOCOR), 4.29 (dd, *J* = 4.5 Hz, 12.0 Hz, 2H, CH₂OCOR), 4.14 (dd, *J* = 6.0, 12 Hz, 2H, CH₂OCOR), 3.62 (t, *J* = 6.5 Hz, 4H, CH₂OH), 2.30 (t, *J* = 7.5 Hz, 6H, CH₂CO), 1.60 (m, 10H, CH₂CH₂CO and CH₂CH₂OH), 1.20 (m, 44H, CH₂), 0.88 (t, *J* = 6.5 Hz, 3H, CH₃). ¹³C-NMR (CDCl₃ 100 MHz): δ 173.09 (COR, *sn*-1, 3), 173.01 (COR, *sn*-1, 3), 172.59 (COR, *sn*-2), 68.94 (CHOCOR), 62.90 (CH₂OCOR), 62.14 (CH₂OH), 34.29, 34.16, 34.13, 32.81, 32.04, 29.82, 29.78, 29.74, 29.60, 29.48, 29.39, 29.31, 29.23, 29.10, 29.07, 28.96, 25.82, 25.80, 24.99, 24.94, 22.83, 14.27 (CH₃). CI-MS: *m/z* 693.6 ([M+Na]⁺).

Triol

¹H-NMR (CDCl₃ 500 MHz): δ 5.26 (m, 1H, CHOCOR), 4.29 (dd, *J* = 4.5, 12.0 Hz, 2H, CH₂OCOR), 4.14 (dd, *J* = 6.0, 12 Hz, 2H, CH₂OCOR), 3.62 (t, *J* = 6.5 Hz, 6H, CH₂OH), 2.30 (t, *J* = 7.5 Hz, 6H, CH₂CO), 1.60 (m, 12H, CH₂CH₂CO and CH₂CH₂OH), 1.20 (m, 24H, CH₂). ¹³C-NMR (CDCl₃ 125 MHz): δ 173.31 (COR,

sn-1, 3), 172.89 (COR, *sn*-2), 68.93 ($\underline{\text{C}}\text{HOCOR}$), 62.86 ($\underline{\text{C}}\text{H}_2\text{OCOR}$), 62.85 ($\underline{\text{C}}\text{H}_2\text{OCOR}$), 62.12 (CH_2OH), 34.19, 34.03, 32.69, 29.22, 29.19, 29.18, 29.16, 28.97, 28.95, 25.69, 25.66, 24.85, 24.81. CI-MS: m/z 583.4 ($[\text{M}+\text{Na}]^+$).

Rheometric Measurements

The viscosities of the polyol samples were measured in shearing mode with the Universal Dynamic Rheometer PHYSICA UDS 200 (Paar Physica USA) with a constant shearing rate of 51.6 s^{-1} . The results are listed in Table 2.

DSC

The TA 2920 Modulated DSC system from TA instruments was used to study the thermal transitions of the polyols. The procedure to record the crystallization and melting curves was as follows. Initially the sample was kept at $20 \text{ }^\circ\text{C}$ for 5 min to reach its equilibrium state and was then heated to $80 \text{ }^\circ\text{C}$ with a rate of $5 \text{ }^\circ\text{C}/\text{min}$ to erase its thermal history. To record the crystallization curve, the sample was cooled down to $-50 \text{ }^\circ\text{C}$ at a constant rate of $5 \text{ }^\circ\text{C}/\text{min}$ and kept at this temperature for 5 min to allow for the completion of the crystallization. The sample was then heated to $80 \text{ }^\circ\text{C}$ at a constant rate of $5 \text{ }^\circ\text{C}/\text{min}$ to record the melting curve.

Refractometry

The refractive index of the materials was determined according to the ASTM D1747-99, using a CARL Zeiss (Germany) refractometer. The results are reported in Table 2.

Hydroxyl and Acidity Values

The hydroxyl numbers of the polyols were determined according to the ASTM D1957-86 and the acidity values were determined according to the ASTM D4662-98. The average values and standard deviations of triplicate measurements are reported in Table 2.

Results and Discussion

Polyols from Canola Oil and their Chemical Identification

In all the FTIR spectra of the collected pure fractions, i.e. saturated TAG, mono-ol, diol and triol, the $1,650 \text{ cm}^{-1}$ characteristic C=C double bond stretch is

reduced to very small bumps, confirming that almost all the double bonds in the canola oil have been reduced. The absorption band centered at $3,300 \text{ cm}^{-1}$ characteristic of hydroxyl group, is missing in the saturated TAG, but appears in the other three samples with a tendency to grow bigger and broader from mono-ol to diol to triol.

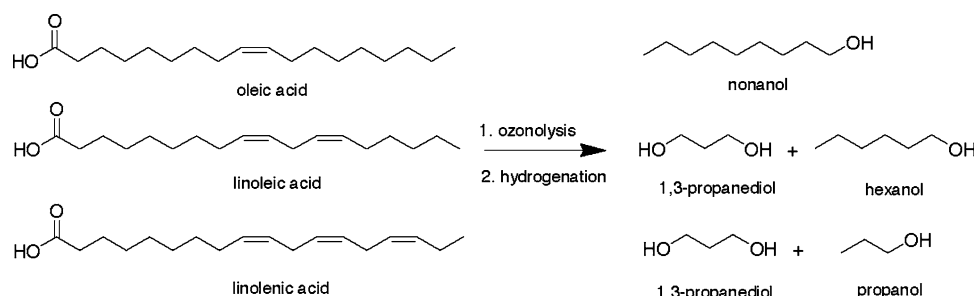
The FTIR indications were confirmed by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$. For triol, the terminal methyl protons and carbon were not observed and for saturated TAG, the methylene protons and carbon adjacent to hydroxyl group were not observed. As for the integration of triplet at 0.88 ppm (representing the terminal methyl groups of the fatty acids), mono-ol was six, and diol was three. For the integration of the triplet at 3.62 ppm (representing the methylene protons adjacent to hydroxyl group), mono-ol was two and diol was four. This indicated that saturated TAG has three fatty acid chains with methyl group at the end of each chain and that triol has three alcohol chains with hydroxyl group at the end of each chain. It also indicated that mono-ol has two fatty acid chains and one alcohol chain and that diol has one fatty acid chain and two alcohol chains.

Samples of saturated TAG, mono-ol, diol and triol were analyzed using HPLC. Each of them demonstrated a single peak with the retention times of 4.04, 5.86, 15.94, and 30.92 min, respectively. The HPLC of the polyol mixture obtained directly after distillation demonstrated four main peaks, with retention times matching those of saturated TAG, mono-ol, diol and triol separately. The mass content of saturated TAG, mono-ol, diol and triol in the Canola-Oxygen Polyol was approximately 10, 20, 46 and 24%, respectively.

Apart from the polyol, some short-chain molecules were also produced as side-products. Figure 3 shows the three possible unsaturated fatty acids in canola (linoleic, linolenic and oleic acids) and the potential short-chain alcohols that can be produced from these materials.

Conveniently, the shorter-chain products were all removed by a single pass in the wiped-blade molecular distillation process. Their separation from the polyols by wiped-blade molecular distillation is desired because, on one hand, all these small side-products are very valuable materials for the chemical industry and on the other hand, mono-alcohols are potential chain terminators to the cross-linking reaction in the production of PUs and short-chain di-alcohols do not add any benefits to PU formation in the heavier polyol mixture (beyond minimal utility as chain extenders). The short-chain molecules were analyzed with GC-FID. Table 1 gives their theoretical and experimental

Fig. 3 Production of potential short chain alcohols by ozonolysis and hydrogenation from possible unsaturated fatty acids (linoleic, linolenic and oleic acids) in canola oil



amounts in grams as well as those of the polyols, produced from 100 g of canola oil. The theoretical values were calculated based on the amount of TAGs compiled by Neff et al. [19] for 100 g of canola oil and by considering that all the double bonds are cleaved.

Physical Properties of the Polyols from Seed Oils

The hydroxyl and acidity numbers and the refractive indices of the canola-oxygen polyol and canola-air polyol are shown in Table 2. Both polyols ended up with relatively high acidity number because the ozonide, the product of ozonolysis, tends to hydrolyze and produce carboxylic acid [10] that cannot be hydrogenated under the conditions employed in our reactions. As expected, since more oxygen is readily available to cleave double bonds during the ozonolysis reaction, the polyol obtained with oxygen as a supply gas had higher hydroxyl and acidity numbers than the polyol obtained when using air. The polyols produced here had relatively lower hydroxyl values than those produced using

other technologies such as epoxidation and hydroformylation, because it produces only primary hydroxyl groups rather than secondary hydroxyl groups which have the possibility of more than one available position on each carbon chain. Theoretically there is a maximum hydroxyl value of 251 mg KOH/g for canola that can be obtained when producing polyol from canola oil by assuming that all of the double bonds are cleaved [19]. The lower than theoretical hydroxyl values obtained for the polyols produced here are due to the molecular diversity of the starting materials as well as to possible incomplete reactions. Mono-ol and diol are produced because the starting TAGs are not constituted only of three unsaturated fatty acids but contain a mixture of saturated and unsaturated fatty acids. They can also be produced if the ozonolysis reaction does not cleave all the double bonds on all the fatty acids. This was evident in the case of ozonolysis with air as the feed gas where the extra saturated fatty acids resulted in a mass of the canola-air polyol higher than the theoretical value (see Table 1).

Table 1 Calculated and experimental amounts in grams of polyol and short chain by-product from 100 g canola (errors are standard deviations, $n = 3$)

	Polyol	Propanol equivalent	Hexanol equivalent	Nonanol equivalent	1,3 Propanediol
Theoretical values	65.3	1.70	7.46	28.60	10.00
Canola-air polyol	76.9	0.44 ± 0.19	2.59 ± 0.29	11.85 ± 1.09	0.72 ± 0.21
Canola-oxygen polyol	56.3	0.28 ± 0.06	4.09 ± 0.18	23.53 ± 0.32	0.59 ± 0.04

Polyol includes saturated TAGs, mono-ol, diol and triol

Propanol equivalent includes the 3-carbon derivatives (propanol and propionic acid)

Hexanol equivalent includes the 6-carbon derivatives (hexanol and hexanoic acid)

Nonanol equivalent includes the 9-carbon derivatives (nonanol and nonanoic acid)

Table 2 Hydroxyl number, acidity number, viscosity, refractive index, and crystallization and melting temperatures (from DSC) of canola polyols (errors are standard deviations, $n = 3$)

	Hydroxyl number (mg KOH/g)	Acidity number (mg KOH/g)	Viscosity at 25 °C (Pa s) ± 5 × 10 ⁻⁴	$n_D^{35} \pm 5 \times 10^{-4}$	Crystallization temperature (°C)			Melting temperature (°C)		
					T_{1C}	T_{2C}	T_{3C}	T_{1M}	T_{2M}	T_{3M}
Canola-air polyol	152.4 ± 0.3	22.9 ± 0.3	0.4527	1.4663	-9.6	2.3		-8.7	-0.7	8.2
Canola-oxygen polyol	176.4 ± 0.5	51.7 ± 0.1	0.9067	1.4658	-25.4	16.8	29.6	-4.5	23.2	39.7

Table 2 summarizes the crystallization and melting temperatures of the polyol samples. Various levels of crystallinity are present, suggesting a promising suitability to processing within current standard PU-forming capital equipment. In the case of canola-oxygen polyol, a higher crystallization peak (29.6 °C) combined with a higher hydroxyl number resulted in a greater viscosity at the same temperature than that of canola-air polyol. Because it could be a barrier to mass transfer of crosslinkers, the presence of crystals at the processing temperature can be either a problem or a benefit, depending on what type of PU is being produced. It affected the viscosity which obviously would result in increased requirements on the shear and pumping systems etc. of a processing plant. However these variances in crystallinity and viscosity can be manipulated well within the plant environment to create PUs with desirable properties. Compared to commercially available polyols, the polyols synthesized here were well within acceptable tolerances for standard capital equipment.

Acknowledgments We thank Andrew Herberling, Riyszard Nowak and Ereddad Kharraz for their invaluable technical assistance. We thank the Alberta Crop Industry Development Fund (ACIDF), the Alberta Agricultural Research Institute (AARI), AVAC Ltd., Natural Sciences and Engineering Research Council (NSERC), the Agriculture and Food Council (AFC), and the Alberta Canola Producers Commission (ACPC) granting agencies for funding portions of this study.

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