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Ozonolysis of Canola Oil: A Study of Product Yields and Ozonolysis Kinetics in Different Solvent Systems

Tolibjon S. Omonov · Ereddad Kharraz · Jonathan M. Curtis

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Abstract The use of ozonolysis has been proposed as a step in the production of vegetable-oil-based polyols as replacements for the equivalent petrochemicals. As part of an evaluation of the commercial viability of ozonolysis, the intermediates and products formed from the ozonolysis of canola oil using different protic and aprotic solvents and solvent mixtures were systematically studied by GC-FID and size-exclusion chromatography with refractive index detection (SEC-RI). It was found that the use of an aprotic solvent (ethyl acetate) leads to the formation of oligomeric ozonolysis products whereas alcohols and/or mixtures of ethyl acetate with alcohols for the ozonolysis of canola oil do not form high molecular weight compounds. In addition, when ethyl acetate is used as the solvent, the formation of carboxylic acids is observed in the early stages of ozonolysis whereas the use of alcohols significantly reduces acid formation. As expected, extending the ozonolysis time led to extensive carboxylic acid formation, especially using ethyl acetate as a solvent. It was found that the optimum time for the complete ozonolysis of canola oil was largely independent of the solvent used for ozonolysis. However, the yield of ozonolysis products differs considerably depending on the solvents employed. Overall, a clear correlation between the ozonolysis time, product yields and the reaction exothermicity was observed.

Keywords Canola oil · Ozonolysis · Oxidative cleavage

Introduction

Currently, there is widespread interest in the use of renewable resources to replace petroleum as a feedstock in the production of polymers. For example, polylactic acid (PLA) polymers produced from starch have become extremely popular due to the many desirable physical properties of the polymer, its biodegradability and the wide availability of the raw material [1]. Vegetable oils are another class of an abundant renewable resource that can be used in the production of other types of polymers. This has been shown for soy oil, now used commercially in making bio-based polyols for polyurethane applications (e.g. see http://www.bioh.com). In Western Canada, as in other parts of the world, canola oil production makes a large contribution to the economy and production in Canada is expected to rise by a third to 15 million tonnes by 2015 [2]. Hence, it is likely that canola producers will be looking to new industrial applications in addition to the traditional food markets, to help utilize this increased production.

Canola oil has a low level of saturated fats (~7%) along with high levels of monounsaturated (MUFA) and polyunsaturated (PUFA) fatty acids [3]. A breakdown of the typical fatty acid and triacylglycerol (TAG) composition of canola oil is given in Fig. 1a, b, respectively.

It can be seen that more than 90% of canola oil consists of MUFA (mostly oleic acid) and PUFA (linoleic and α-linolenic acids), all of which contain carbon–carbon

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T. S. Omonov · E. Kharraz · J. M. Curtis
Lipid Chemistry Group and Lipid Products Research Alberta (LiPRA), Department of Agricultural, Food and Nutritional Science (AFNS), University of Alberta, Edmonton, AB T6G 2P5, Canada

J. M. Curtis (✉)
3-18 F Agricultural/Forestry Centre,
University of Alberta, Edmonton, AB T6G 2P5, Canada
e-mail: jcurtis1@ualberta.ca

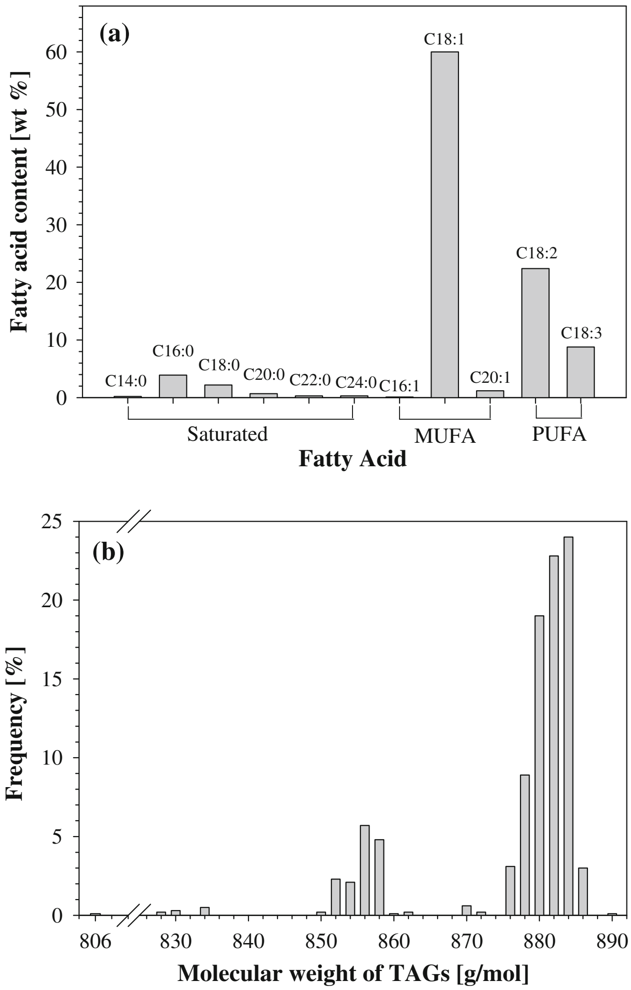


Fig. 1 Fatty acid composition (**a**) and molecular weight distribution (**b**) of canola oil. C14:0—myristic, C16:0—palmitic, C18:0—stearic, C20:0—arachidic, C22:0—behenic, C24:0—lignoceric, C16:1—palmitoleic, C18:1—oleic, C20:1—eicosenoic, C18:2—linoleic, C18:3—α-linolenic. Adapted from [3]

double bonds within their fatty acyl groups which are readily available for chemical/structural modifications especially via oxidation processes.

An important example that has been described in the literature involves the oxidative cleavage of double bonds using ozonolysis reactions. Ozonolysis is a convenient and highly effective method owing to the complete reaction of ozone with the starting material [4] to give an array of compounds, including carboxylic acids, ketones, aldehydes, and alcohols [5]. It can proceed under mild conditions following simple procedures [6]. Ozonolysis achieves oxidative scission of C=C double bonds by a mechanism which has been described in detail elsewhere [7–10]. In brief, ozonolysis of double bonds (Scheme 1) proceeds via the cycloaddition reaction (A) of ozone with the double bond to form a primary molozonide (B) followed by decomposition/cycloreversion of the ozonide to yield an aldehyde and carbonyl oxides (zwitterion, C).

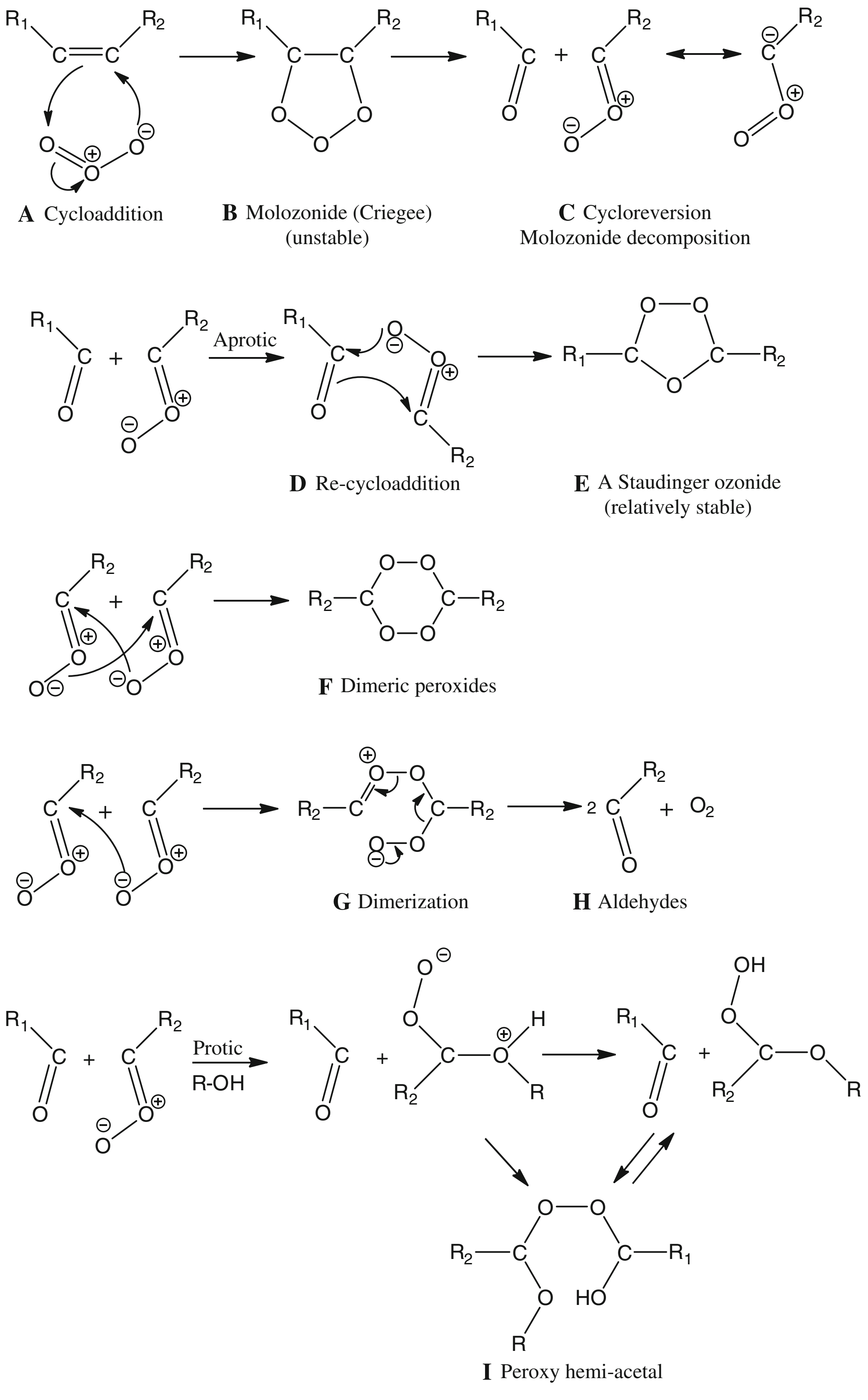
In an aprotic solvent, the products of the decomposition process react with each other (D) to give the more stable an isomeric form of ozonide (E). In addition, formation of oligomeric peroxides (Reaction F) [7, 9, 11] and/or dimers (Reaction G) and secondary aldehydes (Reaction H) [11] were also reported due to the interaction of the zwitterionic species with itself. However, the reactions presented in Scheme 1 do not take into account any interactions with solvents.

In a typical ozonolysis procedure the ozone is bubbled through a solution of oil in a suitable solvent. The outcome of the reaction under such conditions will differ significantly depending on the type of solvents used and the multiple bonds being oxidized. If ozonolysis is carried out in the presence of protic solvents such as alcohols, the formation of alkoxy hydroperoxides [9] and/or peroxy hemi-acetals (see Reaction I) [10, 12] cannot be avoided.

The modification of vegetable oils via oxidative cleavage of their double bonds by ozonolysis has been described in the literature [10, 13–16]. This reaction can lead to the formation of aldehydes [10, 17] and may be followed by a further reduction step to form primary alcohols [15, 18, 19]. It has been reported that unsaturated vegetable oil triacylglycerides can be converted to bio-based precursors for the production of polyurethanes [19–24] and other thermoset resins, such as formaldehydes [10]. A number of examples of the ozonolysis process as a key step for the synthesis of pharmaceutically important compounds are also given in the literature [5].

Several attempts have been made to make aldehydes the primary products by applying an ozonolysis technique for the oxidative cleavage of double bonds of soybean oil [17, 19], rapeseed oil [10] and canola oil [16, 19] using different solvents or mixture of solvents. It was reported that ozonolysis of unsaturated vegetable oils also led to the formation of significant amounts of other products, depending on the type and location of the double bonds. For example, the ozonolysis of canola oil in an aprotic solvent under certain conditions should lead to the formation of propanal, 1,3-propanedial, hexanal and nonanal along with the formation of crude aldehyde oil. These aldehydes can easily be oxidized/transformed into the respective carboxylic acids during a continuous ozonolysis process. However, if alcohols are used as the solvent for the ozonolysis process, the formation of undesirable alkoxy compounds (such as esters and/or peroxy hemi-acetals) between solvent and the ozonolysis products may reduce important functional properties of the product.

Thus, since the desired products for a bio-based precursor for thermoset polymer production from vegetable oils are aldehydes and/or alcohols, the formation of acidic, carbonyl, peroxidic and oligomeric products and side-products may be detrimental to the properties of the final



Scheme 1 Proposed mechanisms of ozonolysis and compounds formed by the ozonolysis of unsaturated fatty acids. Adapted from [7–12]

product. Many studies in the literature present multiple examples of the ozonolysis of vegetable oils and the analysis of the resulting ozonolysis products; however, they have not dealt sufficiently with the ozonolysis kinetics of vegetable oils when employing different solvents.

Clearly, it is important to understand the kinetics of formation of the multiple products during ozonolysis processes as well as the effect of side-products on the product of interest. In addition, a study of the kinetics of the ozonolysis of vegetable oils may facilitate a better understanding of fundamentals of the ozonolysis process itself. Thus, the general objective of this study is to investigate the process of ozonolysis, specifically the products formed during the ozonolysis of canola oil, using different types of solvents, both protic and aprotic.

Materials and Methods

Materials

Food grade canola oil (Loblaws Inc., Canada) was purchased from the local supermarket and was used as supplied. All chemicals were reagent grade or better. Ethyl acetate, anhydrous ethanol (100%) and methanol (99.9%) were purchased from the Fisher Scientific Co and used as solvents for the ozonolysis process. Propanal, propanoic acid, hexanal, hexanoic acid, nonanal, nonanoic acid, methyl nonanoate and ethyl nonanoate (purity $\geq$98%) were purchased from Sigma–Aldrich, and used as calibrating standards for GC-FID. *p*-Anisaldehyde (Sigma–Aldrich) was used as an internal standard for the GC-FID measurements. Tritricosanoin (Mw = 1,101.88 g/mol), distearin (Mw = 625.00 g/mol) and monostearin (Mw = 358.56 g/mol) of purity $\geq$99% obtained from Nu-Chek Prep. Inc. (USA) were used as calibration standards for size-exclusion chromatography with refractive index detection (SEC-RI).

Ozonolysis of Canola Oil

A mixture of canola oil (100 g) and the solvent (600 mL) was placed in a specially designed ozonolysis vessel equipped with a speed controlled motorized mixer and maintained at 0 °C using the temperature controlling unit (Refrigerated/Heating Circulator, Julabo F25). Ozone (concentration is $\sim$50 g/m^3 in the ozone/oxygen mixture) was produced by passing dry oxygen (99.6%, Praxair Canada Inc) as the feed gas through an AZCOZON ozone generator coupled with controller unit (model RMU16-16 and model RMDC-32D & 02, respectively, from AZCO Industries LTD, Canada). The ozone was introduced into the reaction medium as finely dispersed gas bubbles by passing the flow through the specially designed coil, located at the bottom of the ozonolysis vessel. Prior to the start-up series of experiments with different solvents, an optimization of the ozone flow was carried out with canola oil/ethyl acetate mixtures under different flow of ozone and inlet oxygen pressure. An optimum flow of ozone for the ozonolysis of canola oil was found to be 6.5 L/min using an oxygen pressure of 7 PSI and with an agitation speed for the reaction mixture of 500 ± 5 rpm. Thus, all ozonolysis reactions were carried out under these conditions but using different solvents or mixture of solvents. The initial ozonolysis temperature was 0 °C and the total reaction time was 90 min. During the ozonolysis process samples were taken periodically every 10 min (total 10) and analyzed by GC-FID to determine the extent of light fractions of ozonolysis products yield. The change of molecular weight (MW) and MW distribution of canola oil and canola oil ozonides crude fraction was followed by SEC-RI as described below.

Sample Preparation

Solutions of canola oil were prepared in various solvents for ozonolysis. In all the experiments the ratio of canola oil to solvent was kept as 100 g : 600 mL, the initial temperature of the oil/solvent mixture was 0 ± 0.1 °C and the ozonolysis time was 90 min. All ozonolysis experiments were carried out under a constant agitation speed with mechanical stirrers and under a constant ozone flow and oxygen supply. The change in temperature due to the exothermicity of the reaction of ozone with the double bonds of canola oil and other reactions was recorded with an HI 141B (H) thermologger (from Hanna Instruments Canada Inc.), with an accuracy of temperature scanning ±0.1 °C.

To follow the kinetics of product formation during the ozonolysis process, samples were taken every 10 min without interrupting the ozonolysis process. GC-FID was then used to identify and quantify the yield of ozonolysis products. External calibrations based on authentic standards and a *p*-anisaldehyde volumetric internal standard were used to quantify the light fractions of ozonolysis products.

Gas Chromatography (GC-FID)

All GC experiments were conducted using an Agilent gas chromatography system (Model 6890N, Agilent Technologies Inc, USA) consisting of a gas chromatograph equipped with flame ionization detector (FID). A Forte BP 20 capillary column (30 m × 0.25 mm ID, film thickness 0.25 μm, SGE Analytical Science Pty Ltd, USA) was used. The oven temperature was programmed to start at 50 °C and rise to 250 °C at a rate of 10 °C/min. The injector and detector temperature were kept to 250 °C; split ratio: 80:1; injection volume: 1 μL; carrier gas: helium; flow rate 1.5 mL/min, run time: 20.5 min. All data were processed with GC ChemStation (Rev. B.02.01).

Size-Exclusion Chromatography

A 1200 series high performance liquid chromatograph from Agilent Technologies (Agilent Technologies Inc, USA) equipped with an Agilent refractive index detector (RI) was used for all size-exclusion chromatographic experiments to measure MW distributions of the products of ozonolysis. A 79911 GP-500 column (with an average pore diameter ~50 Å, 300 mm length, 7.5 mm ID, and 5 µm particle size, Agilent Technologies Inc, USA) was used under isocratic conditions: mobile phase of dichloromethane (DCM); flow rate 1 mL/min. For every run, the eluent was the same as the sample buffer. The random run-to-run difference in retention times for our system was <0.1%. All data were processed using the Agilent ChemStation for LC 3D Systems (Rev. B.03.01). The SEC calibration curve for the column was carried out using the lipid standards described above.

^{1}H-NMR Spectroscopy

A 400 MHz Varian Inova 400-MR NMR spectrometer was used to examine the structural changes of canola oil and its ozonides. Ozonolysis samples (10 mg) were dissolved in deuterated (D6) acetone (0.7 mL) and kept cold on dry ice prior to NMR measurements. ^{1}H-NMR spectra were obtained at room temperature.

Results and Discussion

The expected product of ozonolysis can be predicted based on the composition of the starting oil. As can be seen in Fig. 1, canola oil consists mainly of oleic (~62%), linoleic (~22%) and α-linolenic (~10%) acids. During the reaction with a TAG containing oleic acid, ozone cleaves the double bond located at the C9 position which can result in a TAG with a 9-carbon primary aldehyde or nonanal or both via secondary reactions as explained in Scheme 1. It should be emphasized that ozonolysis proceeds through an initial formation of the 1,2,3-trioxolanes which dissociate giving an aldehyde plus carbonyl oxide. The final products depend on the balance of the reactions subsequently occurring (Scheme 1). Thus, a lower the yield of the initially formed aldehydes can be a result of a number of reactions including re-cycloaddition forming 1,2,4-trioxolanes, the formation of peroxy hemiacetals and others. Furthermore, other reactions can either convert carbonyl oxides into aldehydes or capture them into other products. The theoretical aldehyde yields given in Table 1 are those that would arise if both double bond carbon atoms were completely converted into aldehydes, which may never be achieved because of these alternative routes, but which provides an informative theoretical maximum value against which to benchmark the observed aldehyde formation. These values are calculated based on the TAG compositions shown in Fig. 1.

In a similar way, linoleic acid would be cleaved at the C9 and C12 positions of unsaturation to yield aldehydes including a TAG with a 9C primary aldehyde chain and the light aldehydes hexanal and 1,3-propanedial. Complete ozonolysis of linolenic acid with multiple double bonds at C9, C12 and C15 can result in two 1,3-propanedial and one propanal molecules as the low MW light fragments. Note that the formation of carboxylic acids due to the ozone attack of aldehydes was not taken into account. However, it is clear that the maximum yield of nonanal (if there is no carboxylic acid formed) or nonanal plus nonanoic acid (in the case of presence of acid) should be equal, as both compounds are formed from the same precursor. The same is true for hexanal/hexanoic acid and propanal/propanoic acid pairs.

Thus, the calculations indicate that the products of the ozonolysis of canola oil should yield up to about 60 wt% of crude aldehyde oil, mostly with three or two aldehyde groups per molecule. A significant amount of low MW chemicals will also be formed (40 wt%) as light aldehydes, predominantly nonanal and 1,3-propanedial. These light aldehydes are also potentially valuable chemicals and can be removed from the crude aldehyde oil using a single pass of wiped blade molecular distillation [18].

Ethyl Acetate as the Solvent

Gas Chromatography (GC-FID) Analysis of Ozonolysis Products Using Ethyl Acetate as the Solvent

Figure 2 shows the GC-FID chromatograms of the volatile components of ozonized canola oil as a function of ozonolysis time using ethyl acetate as the solvent.

The chromatograms shown are normalized to the internal standard (*p*-anisaldehyde, with a retention time (RT) of 14.02 min) with the internal standard peak removed from the chromatograms. Thus, the intensity of the curves and consequently the relative amounts of the ozonolysis products are directly comparable. Since the retention times of the products do not change over the entire ozonolysis period, the curves are represented in a 3D view to illustrate the ozonolysis kinetics.

As can be seen from Fig. 2, the mixture of canola oil with ethyl acetate before ozonolysis (0 min) did not show any traces of chemical components within the relevant RT window. However, ozonolysis of canola oil leads to the formation of nonanal (with RT 6.84 min) and nonanoic acid (RT 15.36 min), even at early stages of the ozonolysis process (10 min). This is expected, since during the ozonolysis process, ozone attacks the double bonds in the canola oil to form ozonolysis intermediates [9], which then form aldehydes and/or carboxylic acids by spontaneous decomposition [15]. An increase in ozonolysis time leads to an increase in the amount of nonanal and nonanoic acid. The formation and gradual increase of hexanal (RT 3.22 min), hexanoic acid (RT 12.0 min) and propanoic

Table 1 Expected products and product yields from the ozonolysis of canola oil, based on the fatty acid distribution illustrated in Fig. 1

Expected ozonolysis products of canola oil	Average molecular weight (g/mol)	Expected yield	
		(mol/L)	(g/L)
Crude aldehyde oil	554.7 (3A)	0.790	438.17
	638.9 (P+2A)	0.158	100.96
	667.0 (S+2A)	0.046	30.78
	723.1 (2P+A)	0.006	3.95
	779.2 (2S+A)	0.004	3.19
	751.2 (SP+A)	0.003	2.38
	Saturates (PPP+SSS+PPS+SPS)	0.001	0.91
Propanal	58.1	0.291	16.87
1,3-propanedial (malonaldehyde)	72.1	1.279	92.18
Hexanal	100.2	0.695	69.60
Nonanal	142.2	1.805	256.80

A aldehyde, *P* palmitic acid, *S* stearic acid

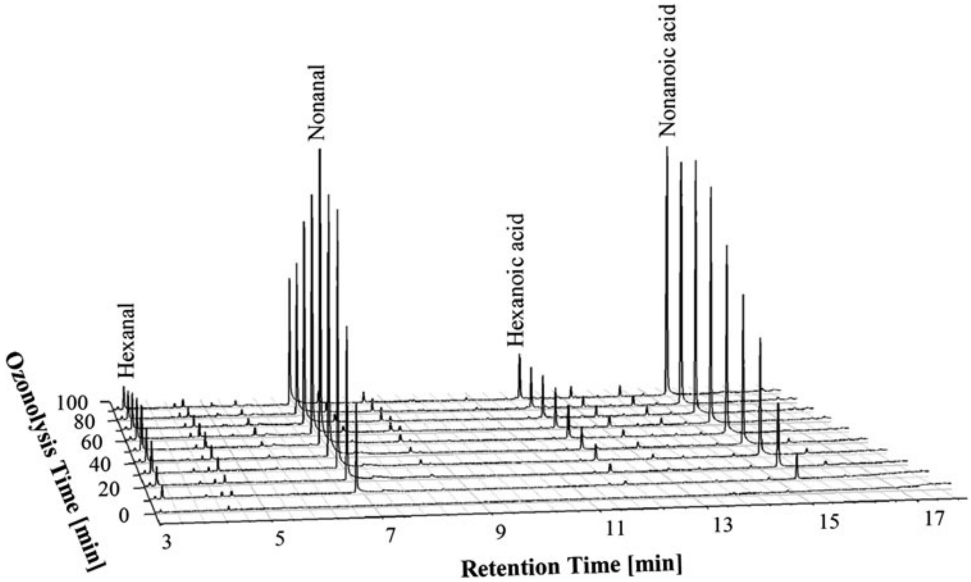


Fig. 2 3D plots of GC-FID chromatograms of canola oil at different stages of the ozonolysis process using ethyl acetate as the solvent

acid (RT 8.5 min) by ozonolysis is also observed (note that the propanal is very volatile aldehyde and could not be observed under the GC conditions used). The trend of increasing intensity of the aldehydes formed (hexanal and nonanal) continues with ozonolysis time until the maximum intensity is observed at ~50 min of ozonolysis. This time can be described as the critical time for the ozonolysis at which all of the double bonds of canola oil have been cleaved, as proven by NMR measurements (see "^{1}H-NMR Spectroscopy of Ozonolysis Products"). A further increase of the ozonolysis time then leads to a decrease in the aldehydes content of the ozonolysis reaction products. Since there are no double bonds left to react with ozone after 50 min of ozonolysis, ozone attack of the aldehydes proceeds resulting in an increasing content of the respective acids (propanoic, hexanoic and nonanoic) with a corresponding decrease of the respective aldehydes. The chromatograms in Fig. 2 highlight the qualitative trend/change of the ozonolysis products; however, an attempt has been made to quantify the relative amount of components in ozonolysis products using an internal standard (*p*-anisaldehyde). It is clear from Fig. 2 that the peaks of individual components are totally resolved from neighboring peaks so that an accurate relative quantification of the components can be performed, as described elsewhere [25, 26].

Kinetics of the Ozonolysis Process with Ethyl Acetate as the Solvent

Although, the product of primary interest is the heavy fraction, i.e. the triacylglyceride derivatives which are the involatile ozonolysis products from canola oil, a study of the light fraction also gives definitive information on the progress of the reaction. The latter can be conveniently monitored by GC, without the added complication of oligomerization to consider.

Figure 3 represents the yields of the ozonolysis products from canola oil, using ethyl acetate as solvent, as a function of ozonolysis time (left-hand *Y*-axes) along with the recorded temperature profile of the reaction mixture (right-hand *Y*-axes). The names of main products of ozonolysis are given as an insert in figure; open symbols represent aldehydes and bold filled symbols are respective acids. The product yields are given in moles per liter of the starting canola oil.

As described above, the major ozonolysis products are nonanal and nonanoic acid due to the fatty acid composition of the starting canola oil. Similar trends in the yield of ozonolysis products are observed as was seen in the peak intensities (retention times) of the individual components. It was expected that the sum of the experimental yields of aldehydes and respective acids should be close to the theoretical values of aldehydes, presented in Table 1. However, the sum of the experimental yields of nonanal and nonanoic acid after 50 min of ozonolysis was about 0.99 mol/L while the theoretical yield of nonanal is 1.8 mol/L. These lower experimental yields of ozonolysis products can be assigned to the presence of ozonolysis intermediates and/or to the formation of oligomeric complexes during the ozonolysis process.

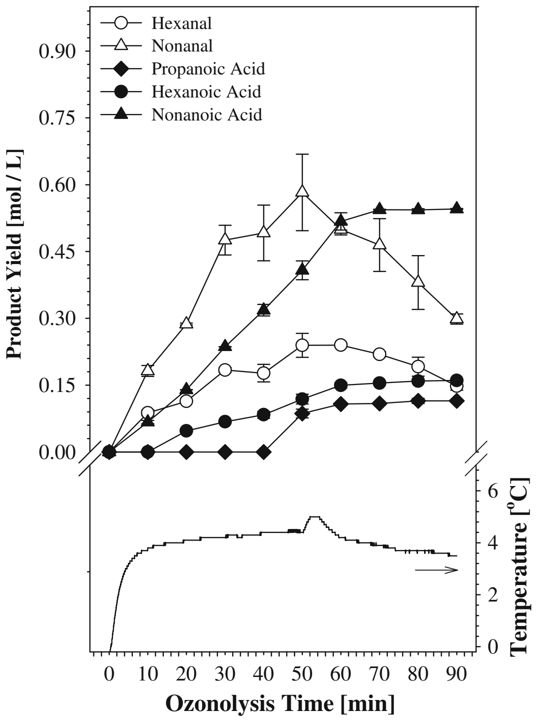


Fig. 3 The ozonolysis products yield and temperature profile during the ozonolysis of canola oil, using ethyl acetate as solvent. *Error bars* represent the standard deviation from at least two runs

Ozonolysis reactions are usually comprised of two exothermic reactions [27] that take place one after the other. The primary reaction is between canola oil and ozone followed by the secondary reaction, a decomposition/stabilization reaction of the intermediate ozonides produced in the primary reaction. Since both of these reactions are exothermic, an attempt was made to find a relationship between the ozonolysis time and heat released by the reaction, by measuring the actual temperature profile of the ozonolysis process. The process temperature was nominally held constant by means of coolant circulating in the jacket of the reaction vessel, held isothermally at 0 °C by a chiller. However, it can be seen in Fig. 3 that a clear relationship was observed between the ozonolysis time and the reaction temperature due to the heat released by the reaction. The trend in kinetics of the reaction has been separated into few steps:

1. 0–10 min: The establishment of a temperature equilibrium between the reactants, the inlet gas (ozone/oxygen) and the chiller. This is accompanied by an increase in temperature of the reaction mass from 0 °C to >4 °C as the exothermic reaction starts.
2. 10–50 min: The ozonolysis reactions reach a steady state as illustrated by the near linear increase in nonanal and nonanoic acid during this time. Under the conditions used, the heat generated by the reactions keeps the reaction temperature at a steady value (∼4 °C) above the coolant temperature. It should be noted that both primary and secondary reactions, described above, contribute to the evolution of heat at this stage.
3. 50–60 min: All of the double bonds of canola oil are cleaved and further reaction with ozone converts aldehydes to carboxylic acids (conversion/decomposition reactions). During this time period, the maximum concentrations of aldehydes are available for further oxidation leading to an enhanced increase in the temperature.
4. 60–90 min: The temperature decreases slowly as the rates of reactions decrease; the ratio of aldehydes to their respective acids continues to change.

Overall, Figs. 2 and 3 and the above discussion demonstrate that there is a relationship between the kinetics of ozonolysis and the yield of light fraction of ozonolysis products.

Size-Exclusion Chromatography of Ozonolysis Products Using Ethyl Acetate as the Solvent

The results from the SEC-RI analysis of the crude canola oil ozonolysis products formed when using ethyl acetate as the solvent, are shown in Fig. 4.

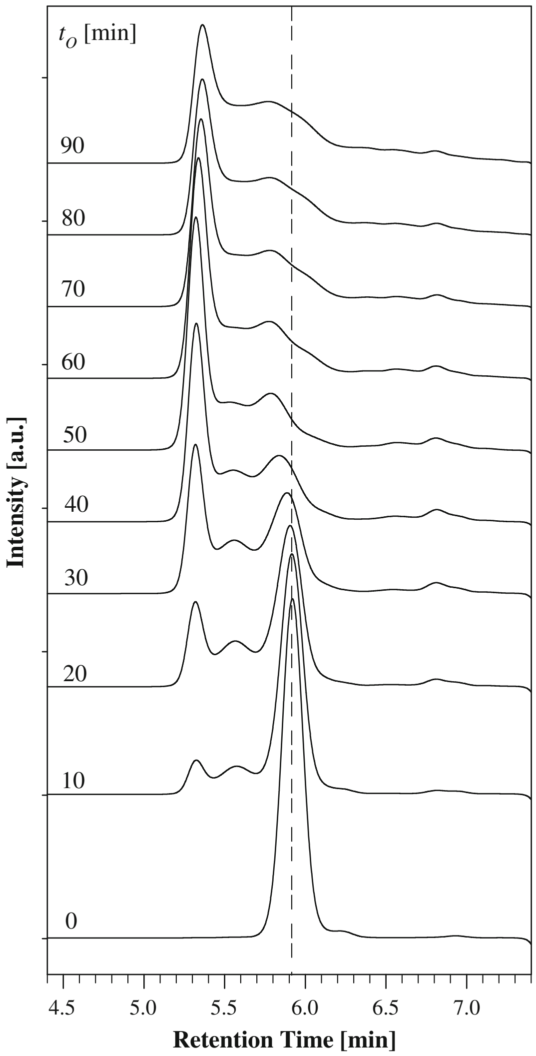


Fig. 4 SEC-RI chromatograms of canola oil at different stages of the ozonolysis process using ethyl acetate as the solvent. The *vertical dashed line* is a guide for the eye, and indicates the retention time of non-ozonized canola oil

SEC-RI analysis of the initial mixture of canola oil with ethyl acetate before ozonolysis produces a single peak, with RT of 5.92 min (MW = 862 g/mol, estimated from SEC-RI trace using MW standards), which is characteristic of canola oil. This result is in agreement with the average MW (879 g/mol) calculated based on the TAG composition of canola oil [3], as presented in Fig. 1b. During the early stages of ozonolysis, the position of this peak remains unchanged but a significant decrease in the peak intensity is observed up to 50 min of ozonolysis. This is indicative of a decrease in the amount of unreacted canola oil due to the ozonolysis reaction. A further increase in ozonolysis time leads to the gradual shift of the RT of canola oil to the lower values (for example, 5.79 min after 90 min), due to ozonide formation, as shown in Scheme 1B, E. Assuming that the average functionality of canola oil is 3.9 (or 0.45 mol double bonds/100 g canola oil [28]) and that all of the double bonds were cleaved during ozonolysis, an increase in MW from ~879 to ~1,066 g/mol (i.e. 879 + 3.9 × 48) is predicted for formation of ozonides. This compares well to the measured MW of approximately 1,089 g/mol for the peak at RT 5.80 min. The change in this peak intensity after 50 min of reaction time is negligible, suggesting that almost all the double bonds of the canola oil have been cleaved. This finding is in good correlation with the GC-FID results of the light fractions, the temperature kinetics of the ozonolysis process described above, and the NMR data described below.

Interestingly, an increase in low MW peaks, as would be expected for the formation of TAG containing 9-carbon primary aldehydes following ozonolysis, was not observed. Instead, ozonolysis led to the formation of high MW compounds even at the early stages of ozonolysis. For example, after 10 min of ozonolysis, a well resolved peak with RT 5.31 min (MW = 3,070 g/mol) and an intermediate peak with RT 5.56 min (MW = 1,815 g/mol) appeared. These two peaks have MWs consistent with trimers and dimers of the ozonolysis intermediates of canola oil, respectively. The basic mechanisms of the oligomeric and/or oligoperoxidic compounds during the ozonolysis processes are described elsewhere [9–11] and presented in Scheme 1F, G. Several studies reported the formation of high MW compounds by the ozonolysis of double bonds of alkenes and enol ethers [29, 30] or vegetable oils [31]. It was also shown that these oligomers could be a result of polymerization of the carbonyl oxide [9], *trans* isomers of ozonolysis products [32, 33] or aldehydes [34] through the variety of different oxygen linkages. In addition, they may have either cyclic [34] or open-chain linear structures [35]. Oligomers derived from the ozonolysis in non-participating (aprotic) solvents were reported to contain peroxidic structures derived from carbonyl oxide and/or structures with hydroperoxide end groups [36]. In general, although oligomers have been reported as being significant reaction products from ozonolysis occurring in solution, the characterization of these oligomeric products has involved a degree of speculation because of the lack of straightforward observation of these oligomers. Hence, identifying the precise structures has proven very difficult [36].

In summary, the formation of high molecular compounds is due to the oligomerization of ozonolysis products of canola oil. These oligomeric products may have very complex structures even starting with discreet low MW alkenes [36]. This situation is further complicated by the additional structural complexity arising from the distribution of TAG molecules present in canola oil prior to reaction. Note that the peak position, and hence average MW, of trimers (RT 5.31 min) did not change up to 50 min of ozonolysis. Furthermore, the intensity of this peak is increased dramatically with ozonolysis time, achieving a maximum at 50 min of ozonolysis. A further increase in the ozonolysis time led to the gradual decrease in the average MW of the trimer peak (MW = 2,756 g/mol, at 90 min) accompanied by a gradual increase in polydispersity, seen as peak broadening in Fig. 4. This could be due to formation of oligomers from products arising from more advanced stages of ozonolysis or perhaps due to further reactions of the abundant trimers formed prior to 50 min. It is surely significant that ozonolysis time at which the maximum concentration of oligomers is observed (50 min) also corresponds both to the time for maximum hexanal and nonanal concentration and the maximum temperature of the reaction mixture.

The results of the SEC/RI experiments of the ozonolysis products of canola oil are presented in Appendix as supporting material where the trends in the SEC/RI traces are given as 3D renderings to further illustrate oligomer formation.

Thus, clear correlations between the product yields of the light fractions (by GC-FID) and crude fractions (by SEC-RI) of the canola oil ozonolysis products and temperature profile of the ozonolysis process (kinetics) have been demonstrated. Under the conditions described, the optimum ozonolysis time for the canola oil using ethyl acetate as a solvent was found to be 50 ± 3 min where all of the double bonds of the canola oil TAG are considered to be cleaved. The use of neutral (aprotic) ethyl acetate for ozonolysis is desirable as canola oil is completely soluble in ethyl acetate and the access of ozone to the double bonds is not hindered by the physical coagulation, precipitation or separation of canola oil.

^{1}H-NMR Spectroscopy of Ozonolysis Products

In "Kinetics of the Ozonolysis Process with Ethyl Acetate as the Solvent" and "Size-Exclusion Chromatography of Ozonolysis Products Using Ethyl Acetate as the Solvent" the critical (or optimum) time of ozonolysis of canola oil was described as 50 ± 3 min where all of the double bonds of the canola oil TAG are considered to be cleaved. Although a consistent end-point for ozonolysis has been observed in experiments using different techniques, these observations are indirect and it is desirable to directly observe the loss of double bonds and formation of ozonides in order to prove this hypothesis. Thus, ^{1}H-NMR spectra were used to examine the structural changes to canola oil TAG during the ozonolysis process. Samples were taken every 10 min from the reaction mixture, diluted in deuterated acetone and kept cold prior to analysis. Figure 5 shows the part of ^{1}H-NMR spectra of canola oil at different stages of ozonolysis which used ethyl acetate as the solvent.

The ^{1}H-NMR spectrum of canola oil (before ozonolysis) shows triplets centered at 5.335, 5.347 and 5.359 ppm, which were assigned to the protons attached to double-bonded carbon atoms (C=C) in the fatty acid chain [37]. As can be seen from the Fig. 5, these double bond peaks decrease in intensity as the ozonolysis time increases. It can be seen that after 50 min of ozonolysis, the ^{1}H-NMR peak associated with the double bond has completely disappeared. This result confirms the conclusions of the GC-FID and SEC-RI experiments i.e. show that all of the C=C double bonds have disappeared in 50 min.

On the other hand, the ozonolysis of canola oil produces ozonides (see Scheme 1, reaction E) resulting in new resonances centered at 5.137 and 5.196 ppm, previously assigned [38] to the protons in the 1,2,4-trioxolanes. The peak in this region at 5.262 ppm is produced by the methine proton of the glycerol [37]. As can be seen from

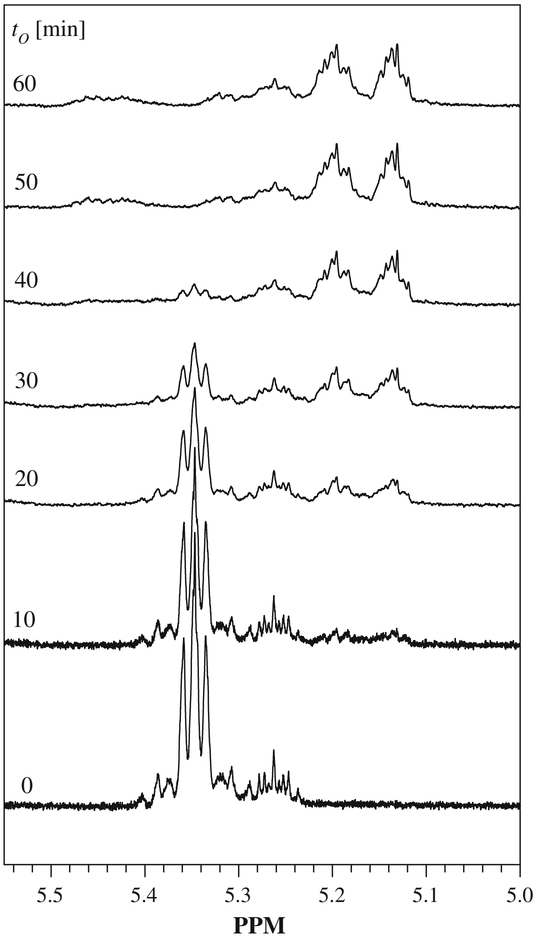


Fig. 5 ^{1}H-NMR spectra of canola oil at different stages of the ozonolysis process, using ethyl acetate as a solvent. Resonances at 5.335, 5.347 and 5.359 ppm are associated with carbon–carbon double bonds and resonances at 5.137 and 5.196 ppm are related to ozonides

the figure, there is a direct relationship between the intensities of the resonances relating to double bonds and ozonides i.e. the ozonide abundance increases with ozonolysis time whilst the abundance of the remaining double bonds decreases. Thus, the extent of ozonolysis can be either monitored either by chromatographic (GC-FID and/or SEC-RI) experiments which detect the reaction products, or using direct ^{1}H NMR measurements which show the concurrent loss of double bonds and formation of ozonides.

Alcohols as the Solvents

If participating/reacting solvents, such as alcohols, are used in the ozonolysis processes they will react chemically with the ozonide intermediates. The formation of alkoxy-, acyloxy- and hydroxyl- hydroperoxides using reactive solvents for the ozonolysis are described and tabulated in [7].

GC-FID Analysis of Ozonolysis Products Using Alcohols as the Solvents

Figure 6 shows the GC-FID chromatograms of canola oil at different stages of the ozonolysis process when using either methanol (Fig. 6a) or ethanol (Fig. 6b) as the solvent.

The chromatograms show that the major volatile product of the ozonolysis of canola oil in alcohols is nonanal, with RT 6.84 min. However, the use of methanol as a solvent also leads to the formation of the ester methyl nonanoate (RT 7.97 min, Fig. 6a) by reaction of the primary ozonide intermediates with methanol. This may involve the reaction of carbonyl oxides to form alkoxy hydroperoxides and elimination of water. Similarly, use of ethanol as the solvent results in the formation of ethyl nonanoate with RT 8.47 min (Fig. 6b). Very significantly, the formation of carboxylic acids (propanoic, hexanoic and nonanoic acids with expected RT of 8.5, 12.0 and 15.36 min, respectively) is completely depressed at the early stages of ozonolysis (compare Fig. 2 with Figs. 6a, b) until up to 50 min of ozonolysis time. A further increase in the ozonolysis time beyond this point did lead to the formation of small amount of carboxylic acids in both systems, but the amount of acid formed was still significantly lower than in the system where ethyl acetate was used as the solvent. Since it is known that the alcohols are very reactive towards ozone [39], the observed decrease in the oxidation of aldehydes to carboxylic acids in the presence of alcohols is most is likely due to the preferential oxidation of those alcohols by ozone over the oxidation of aldehydes. Hence, when using methanol or ethanol as the solvent, the formation of formic and acetic acid dominate over the formation of carboxylic acids from oxidation of the light ozonolysis products.

Overall, a slightly higher yield of nonanal and a smaller amount of nonanoic acid was observed in the system with ethanol, compared to that with methanol. Furthermore, the yield of the ethyl nonanoate was smaller than the yield of methyl nonanoate. Thus, of the three solvents tested, ethanol is the preferred choice in order to minimize the formation of carboxylic acid and ester by-products.

Kinetics of the Ozonolysis Process with Alcohols as the Solvents

Figure 7 shows the molar yield of ozonolysis products formed from canola oil in either methanol (Fig. 7a) or ethanol (Fig. 7b) as a function of ozonolysis time. The temperature profile (right-hand *Y*-axes) of the ozonolysis process is also integrated into Fig. 7 for easy navigation.

As described above, the main volatile product of the ozonolysis of canola oil in alcohols is nonanal. For both methanol and ethanol, the yields of aldehydes (hexanal and nonanal) are slightly higher compared to the ethyl acetate/canola oil based system, but significantly lower levels of carboxylic acid were also observed. For both methanol and ethanol systems, the yield of the ozonolysis products goes through a maximum at ~50 min, as can be seen in Fig. 3 for the ethyl acetate based system. This time can be described as a critical time for ozonolysis, when all of the carbon–carbon double bonds in the canola oil have been cleaved. Thus, it appears that using the ozonolysis conditions and reaction vessel design applied in this work, the critical time for ozonolysis does not depend on the solvent employed (methanol, ethanol, ethyl acetate).

The temperature profiles of the ozonolysis process with alcohols were found to be slightly different from the system with ethyl acetate as a solvent. As can be seen from Fig. 7a, b the initial trend in temperature profile is similar to the ethyl acetate based system (Fig. 3) up to 50 min of ozonolysis. After this, further increases in ozonolysis time led to a marked decrease in the temperature of the reaction mixture for both alcohols. Assuming that no carbon–carbon double bonds are left after this critical time of ozonolysis (50 min), the heat released after the critical time can be associated with the decomposition/stabilization processes i.e. the further oxidation of aldehydes and oligomeric compounds formed during the ozonolysis process. The contribution of heat released from the oxidation of aldehydes by ozone to form carboxylic acids is low, as indicated by the low amount of carboxylic acid formed. In contrast, the amount of carboxylic acids formed in the ethyl acetate based system was much higher (Fig. 2), as was the heat released (Fig. 3).

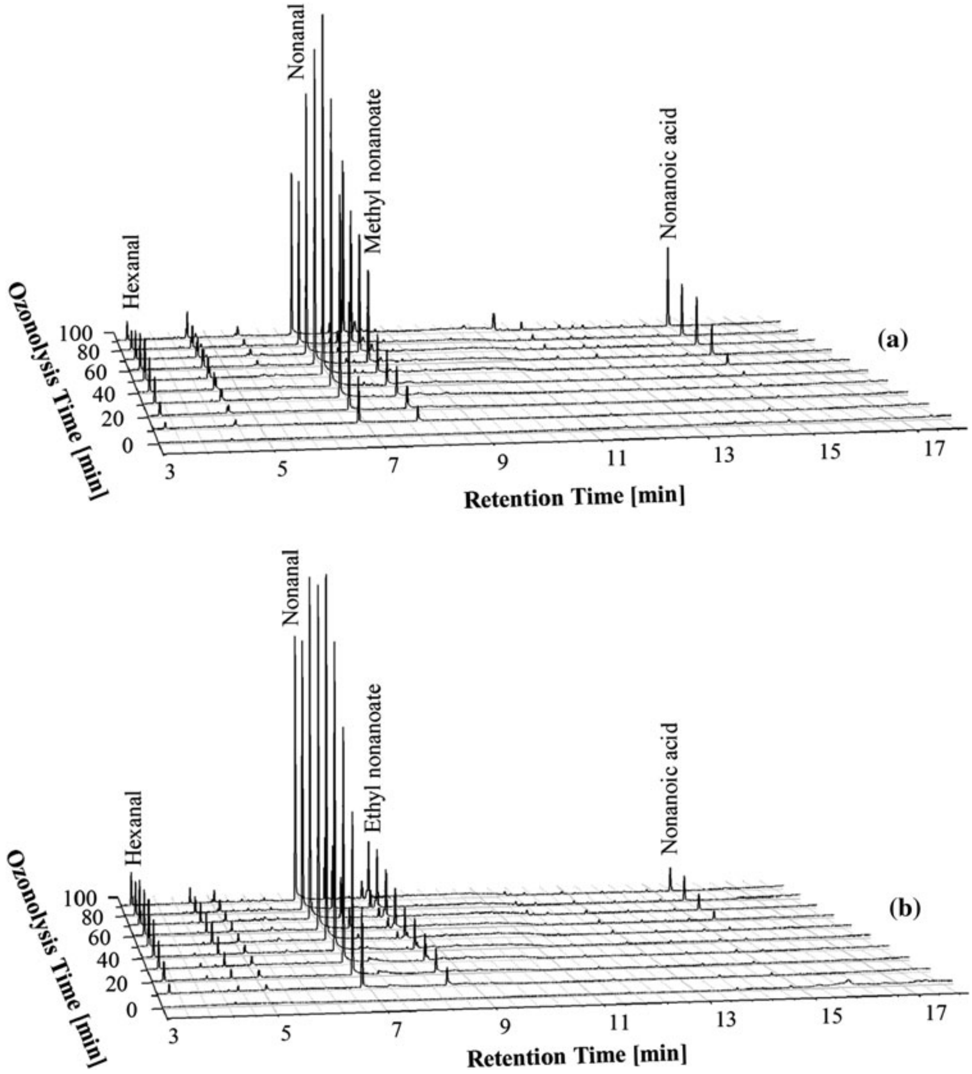


Fig. 6 3D plots of GC-FID chromatograms of canola oil at different stages of the ozonolysis process using methanol (**a**) and ethanol (**b**) as the solvents

SEC-RI Analysis of Ozonolysis Products with Alcohols as the Solvents

Figure 8 shows the SEC-RI chromatograms of the ozonolysis products from canola oil at different stages of the ozonolysis process, using methanol (Fig. 8a) or ethanol (Fig. 8b) as a solvent.

It can be seen from Fig. 8 that the mixture of canola oil with either methanol or ethanol gives rise to a single peak (MW = 856 g/mol), which is characteristic of canola oil and similar to that seen at the $t = 0$ time point for the ethyl acetate based system (see Fig. 4). Remarkably, in Fig. 8 there is almost no evidence for the formation of higher MW oligomeric substances, in sharp contrast to that seen when ethyl acetate is the solvent (Fig. 4). Using either methanol or ethanol, no significant changes are observed in the peak position during the first 50 min of ozonolysis. However, for the methanol based system a slight decrease of MW (shift of peak position to a higher elution volume/longer retention time) was observed after this period (Fig. 8a). In contrast, the ethanol based system (Fig. 8b) does not show any shift in the peak position, and consequently the average MW does not change beyond 50 min. A second difference that is observed between the SEC traces in Fig. 8 is that there is consistently greater polydispersity (i.e. peak width) for the ethanol system, most prominently seen as a an unresolved tail at shorter retention times indicating a small amount of material of greater MW than the starting triacylglycerides. For both systems, a decrease in peak intensities is observed up to 50 min of ozonolysis time but no further decrease was observed with longer ozonolysis times. This implies that all double bonds are cleaved by 50 min, consistent with conclusions from the GC data.

The formation of oligomeric compounds was negligible using both alcohols as solvents. It has long been known that methanol and ethanol are the most reactive solvents toward ozonolysis [39]. Furthermore, it has been shown that if

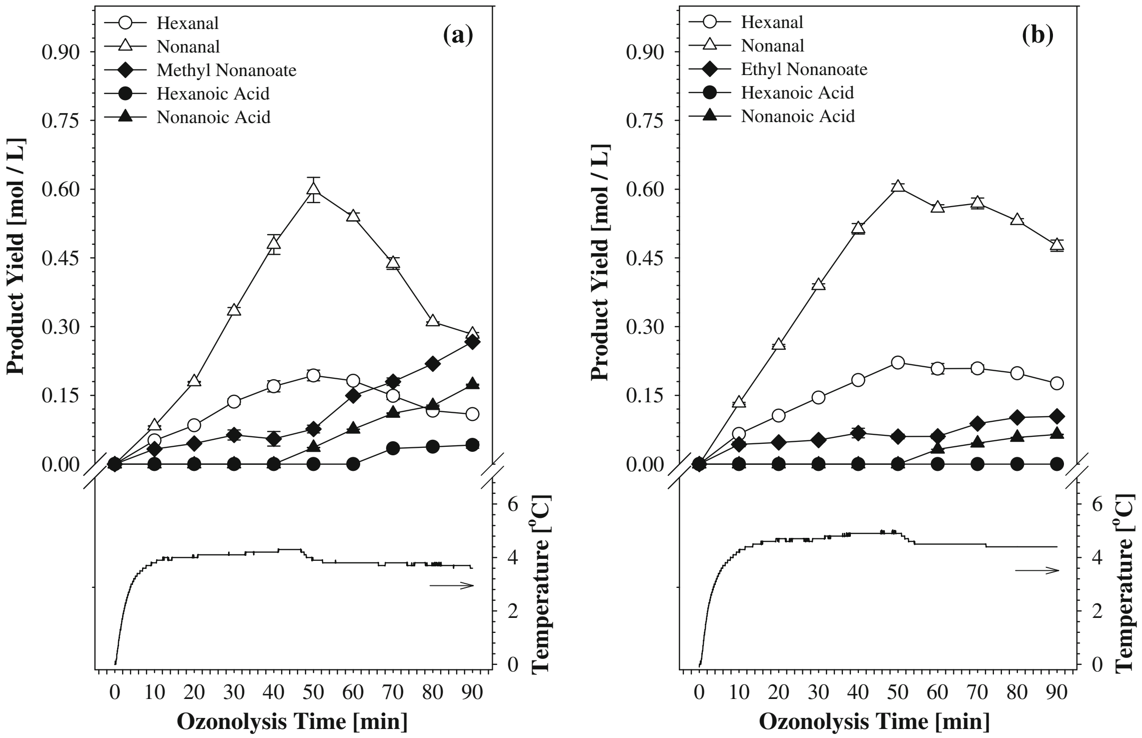


Fig. 7 Kinetics of the ozonolysis products yield and temperature profile of ozonolysis process of canola oil using methanol (**a**) and ethanol (**b**) as solvent. *Error bars* represent the standard deviation from at least two runs

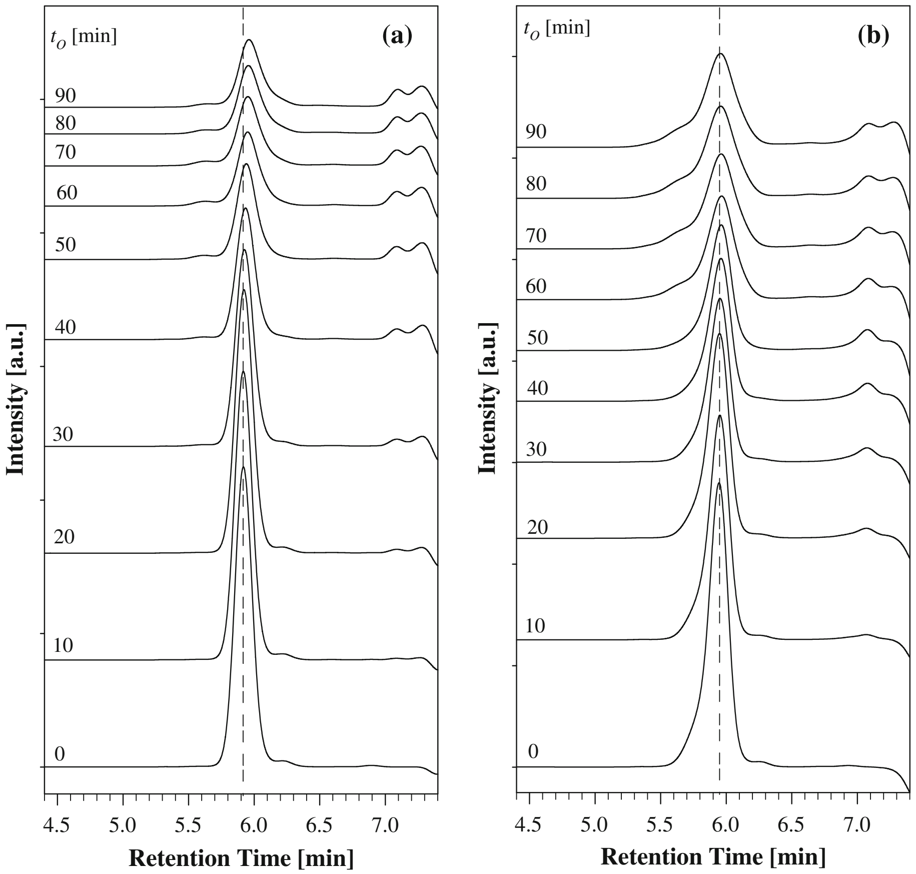


Fig. 8 SEC-RI chromatograms of canola oil at different stages of ozonolysis process using methanol (**a**) or ethanol (**b**) as the solvent. The *vertical dashed line* is guide for the eye, and indicates the retention time of non-ozonized canola oil

ozonolysis of an alkene is carried out in excess alcohol, the zwitterion intermediate can be trapped in the form of an alkoxy-hydroperoxide [40] or a peroxy hemi-acetal (Scheme 1I). These mechanisms tend to reduce the progress of further reactions beyond the formation of aldehydes. In contrast, when non-participating solvents are used, further reactions that result in the formation of carboxylic acids, along with the formation of oligomeric substances via condensation reactions involving peroxides, occur abundantly.

There exists an apparent inconsistency between the SEC data and the assumption that ozonolysis cleaves the carbon–carbon double bonds on the fatty acyl groups to produce, for example, nonanal and a triacylglyceride with 1, 2 or 3 oleic acid moieties replaced by 9C primary aldehydes. If the latter were the only reaction occurring then one would expect to observe a shift in the TAG peak position to longer retention times due to a significant decrease in MW. With ethyl acetate (Fig. 4) there is a clear shift in intensity from the TAG peak to the oligomer peak at ~5.3 min indicating that any involatile aldehydes rapidly oligomerize. This is consistent with published data [18, 41] where drastic hydrogenation conditions are required to convert the oligomeric products of ozonolysis into poly-hydroxy compounds (polyols)—this would not be expected if pure aldehyde oil were present. On the other hand, with methanol or ethanol there is almost no shift in TAG peak position which suggests that the TAG MW remains unchanged although its intensity decreases. This could be explained if reactions were occurring which convert the TAG into methyl or ethyl esters. In fact the formation of methyl or ethyl nonanoate is seen in the GC data (Fig. 6) starting from the first measurement once ozonolysis has started (i.e. $t = 10$ min) although this could also arise via the further oxidation of nonanal to nonanoic acid followed by esterification with the solvent. However, the general lack of shift in the TAG peak in the SEC traces could be because as the TAG is converted to aldehydic form, further adductions by the alcohols occur, resulting in similar MWs.

Use of Solvent Mixtures

From the above discussion it can be concluded that using methanol or ethanol as solvents for the ozonolysis of canola oil might be preferable over ethyl acetate in order to minimize acid and oligomer formation. In addition, some of the ozonolysis intermediates including alkoxy peroxides are converted to aldehydes. However, the overall yield of ozonolysis products remains relatively low compared to the values given in Table 1. The theoretical maximum yield of nonanal from canola oil, with no nonanoic acid formation, is approximately 1.8 mol/L. In contrast, the actual yield of C_9 fragments arising from canola oil after 50 min of ozonolysis using ethyl acetate is 0.99 mol/L, compared to 0.71 mol/L for methanol and 0.66 mol/L for ethanol. Note that since nonanoic acid is formed by the oxidation of nonanal [42], then the total amount of nonanal formed during ozonolysis in the presence of ethyl acetate is actually the sum of the amounts of nonanal and nonanoic acid. In addition, the actual yields of C_9 fragments using alcohols as solvents also include the yields of methyl- and ethyl-nonanoates. It can been seen with reference to Figs. 3 and 6 that at around 50 min, when the oxidation of the carbon–carbon double bonds is complete, the total molar yield of nonanal plus nonanoic acid is higher using ethyl acetate than alcohols as solvents, but the overall yield is still well below the theoretical maximum value of 1.8 mol/L. Thus, not all primary ozonolysis intermediates become aldehydes, regardless of solvent. This is quite consistent with the examples of competing reactions shown in Scheme 1 and discussed above, which trap aldehydes or inhibit their formation.

GC-FID of Ozonolysis Products Using Mixtures of Solvents

Finally, an attempt was made to use a combination of protic and aprotic solvents for the ozonolysis of canola oil. This approach is not new having been previously applied to the ozonolysis of soybean oil [17] or rapeseed oil [10]. However, these previous studies focused on the analysis of the final product rather than on following the progress of these reactions.

Figure 9a, b shows the GC-FID chromatograms of the volatile components formed from canola oil at different stages of ozonolysis when using 90/10 v/v mixtures of (a) ethyl acetate/methanol or (b) ethyl acetate/ethanol as the solvents.

Similar products were observed as seen in the systems with alcohols alone but for both mixed solvent systems (a) and (b) the yields of aldehydes (the desired product) were significantly higher reaching their maximum values (0.88 and 0.82 mol/L with methanol and ethanol, respectively) after 50 min of ozonolysis (Fig. 10a, b).

This result can be explained as follows: the presence of ethyl acetate (in which canola oil and ozonolysis products are soluble) leads to efficient ozonolysis due to the miscibility of canola oil in this solvent. At the same time, the presence of alcohol prevents the formation of unwanted carboxylic acids by trapping zwitterions in alcohols [40] thus forming esters and/or by absorbing ozone [39] as discussed above. However, a further increase of the ozonolysis time (60 min and more) leads to a dramatic increase in the formation of carboxylic acids. For example, in Figs. 9 and 10 it can be clearly seen that after 50 min the nonanal concentration decreases as dramatically as the

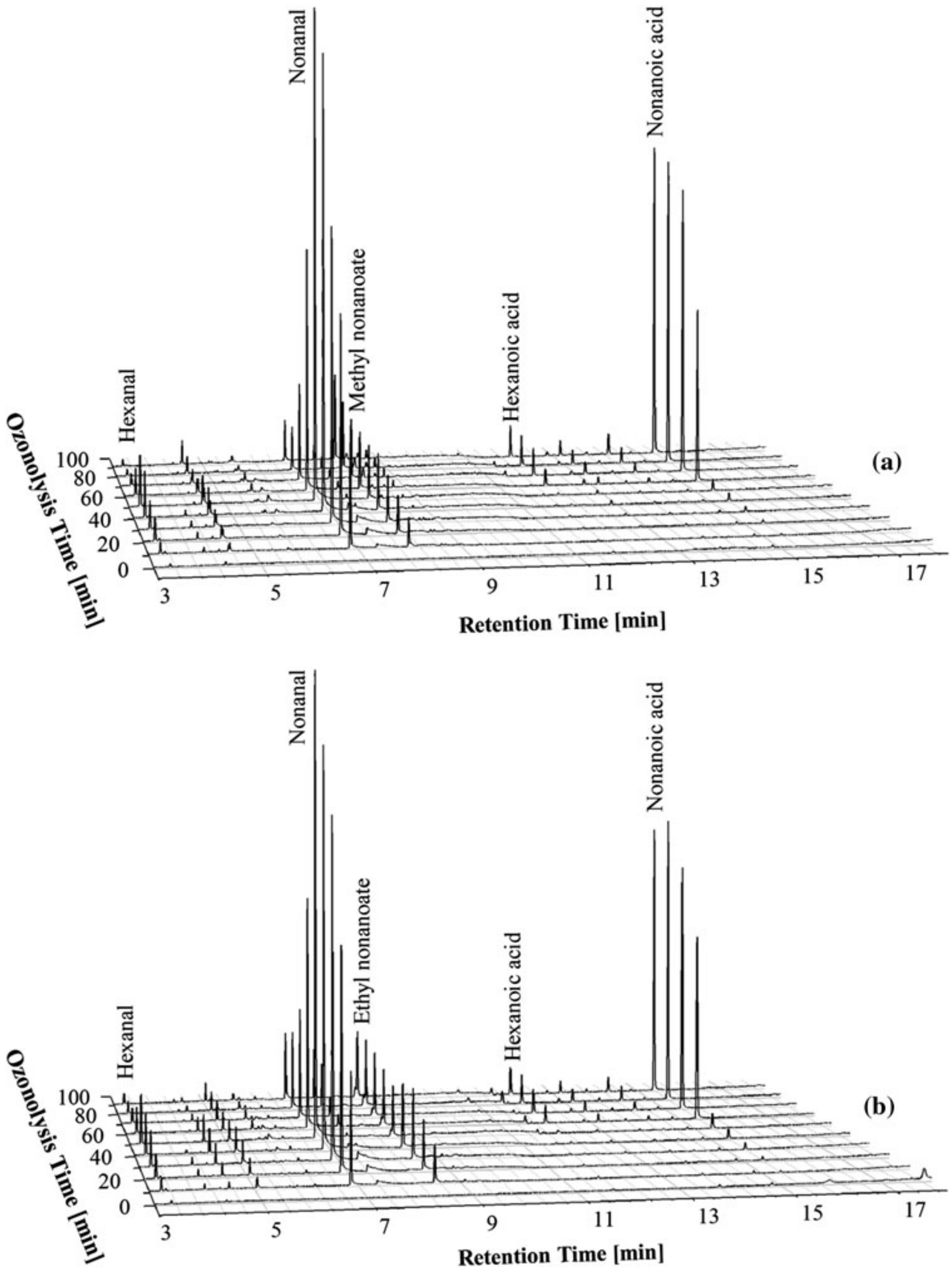


Fig. 9 3D plots of GC-FID chromatograms of canola oil at different stages of the ozonolysis process using the mixture 9:1 v/v of ethyl acetate/methanol (**a**) and 9:1 v/v of ethyl acetate/ethanol (**b**) as the solvents

nonanoic acid concentration rises. This is because the critical time for ozonolysis has been reached and beyond this all further ozone is utilized to form secondary ozonolysis products (carboxylic acids).

This suggestion is also consistent with the observed changes in the reaction temperature during the ozonolysis process. A large surge in temperature was observed after 50 min of ozonolysis. This peak in the temperature profile is associated with the heat released during the rapid carboxylic acid formation reactions. The temperature profile then eventually reaches another equilibrium state at long times as the amount of aldehyde available reaction reaches a minimum value.

Thus, the products of the ozonolysis of canola oil in an ethyl acetate/alcohol mixture are a combination of those seen in the individual solvents. In other words, the high yield of aldehydes is associated with the presence of ethyl acetate, whereas the low production of carboxylic acids along with the additional formation of esters, is associated with the presence of alcohols.

SEC-RI Results of Ozonolysis Products Using Mixtures of Solvents

Figure 11 shows the SEC-RI chromatograms of ozonized canola oil at different stages of ozonolysis when using 90/

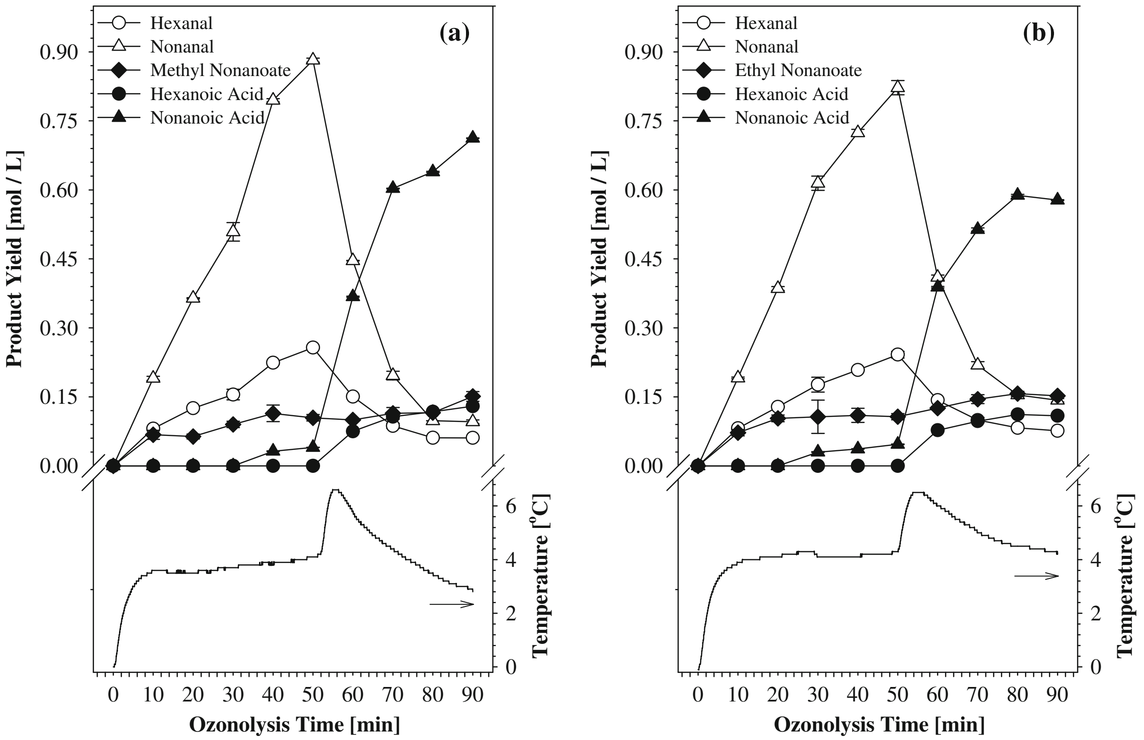


Fig. 10 The ozonolysis products yield and temperature profile during the ozonolysis of canola oil using the mixture 9:1 v/v of ethyl acetate/methanol (**a**) and 9:1 v/v of ethyl acetate/ethanol (**b**) as the solvents. *Error bars* represent the standard deviation from at least two runs

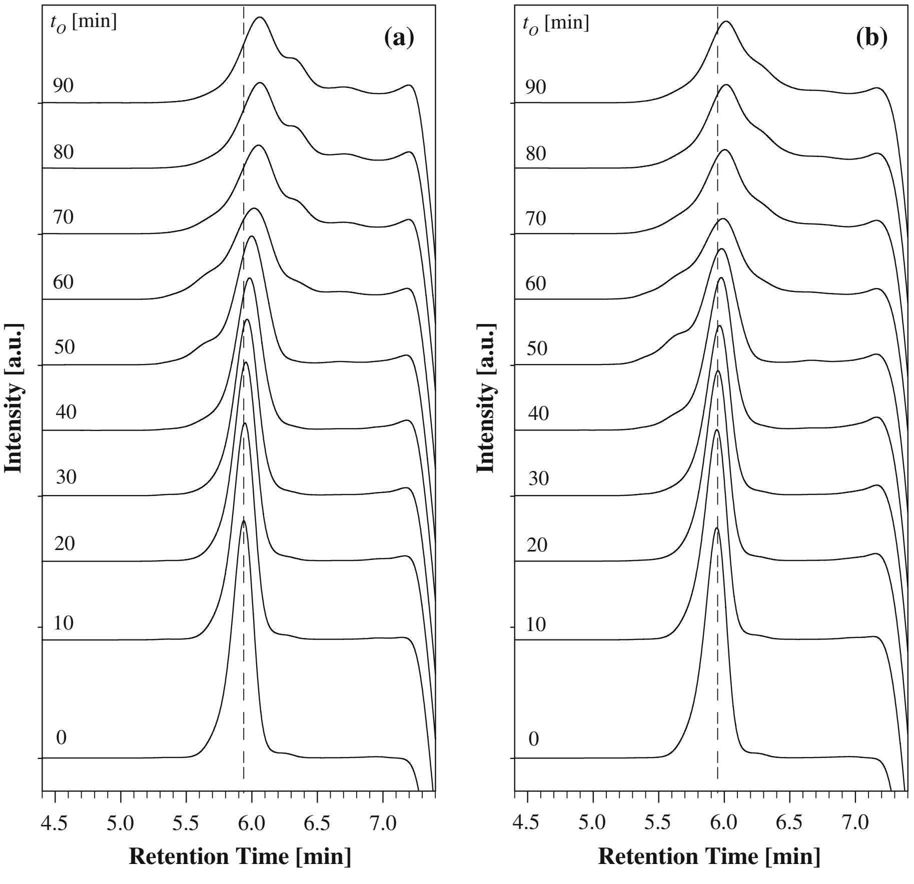


Fig. 11 SEC-RI chromatograms of canola oil at different stages of the ozonolysis process using the mixture 9:1 v/v of ethyl acetate/methanol (**a**) and 9:1 v/v of ethyl acetate/ethanol (**b**) as solvent. The *vertical dashed line* is guide for the eye, and indicates the retention time of non-ozonized canola oil

10 v/v mixtures of (a) ethyl acetate/methanol or (b) ethyl acetate/ethanol as the solvent.

It can be seen from Fig. 11 that for these systems a single peak with RT 5.94 (MW = 875 g/mol), characteristic of canola oil, is observed up to 50 min. This value is comparable to that seen where the pure solvents were used. For both solvent mixtures used, a gradual increase in the peaks RT during was observed with increasing ozonolysis time. The estimated average MW after 90 min of ozonolysis was MW = 680 g/mol for the ethyl acetate/methanol system, and MW = 730 g/mol for the ethyl acetate/ethanol system. These differences in the average MW of the final products of ozonolysis can be explained by the differences in MW between the participating solvents. In addition, for both systems the formation of small amounts of high MW compounds are observed as a shoulder to the main peak after 50 and 60 min of ozonolysis. These peaks, presumably dimers, disappear on further ozonolysis, presumably through decomposition processes. In addition, the formation of low MW fractions with an average MW = 370 g/mol for ethyl acetate/methanol and MW = 408 ± 3 g/mol ethyl acetate/ethanol systems is observed. These likely arise through condensation reactions involving the light components of the ozonolysis products and possibly include the alcohol. For both systems, a gradual change in the peak intensity was observed up to 50 min of ozonolysis time when all the carbon–carbon double bonds have been cleaved. Beyond this, a further increase in the ozonolysis time did not alter the peak areas observed.

Conclusions

The effect of the solvent on the kinetics and of the ozonolysis of canola oil has been investigated using methanol, ethanol, ethyl acetate and ethyl acetate/alcohol mixtures under similar experimental conditions. It was found that the choice of solvent or solvent mixture greatly affects the yields and types of reaction products obtained from ozonolysis. Most significant for the use of ozonolysis as a reaction step in the industrial production of polyols, the choice of solvents was shown to major impact on the amount of oligomeric ozonides formed which in turn greatly hinders their conversion to polyols. Canola oil has a high solubility in ethyl acetate which at first appears to be a suitable solvent for ozonolysis. However, the facile formation of oligomeric compounds and carboxylic acids during ozonolysis limits the usefulness of ethyl acetate as a solvent if the products of interest are aldehydes. Note that the use of reactions that attempt to liberate aldehydes from ozonides (e.g. zinc in the presence of acetic acid) were not considered in this study since the focus was on the ozonolysis process itself. The use of alcohols (methanol and ethanol) as solvents in the ozonolysis of canola oil gives comparable yields of the ozonolysis products as was obtained using ethyl acetate along with a significant decrease in the amount of carboxylic acids formed. However, the formation of esters may reduce the yield of aldehydes available for further chemical modification.

The most appropriate solvent for the ozonolysis of canola oil or other vegetable oils was found to be a mixture of aprotic (ethyl acetate) and protic (methanol or ethanol) solvents, where the oil is fully soluble in the former solvent and the intermediates are reactive toward the latter one. This results in the maximum yield of desirable ozonolysis products that can be achieved, along with the minimum production of unwanted carboxylic acids due to the presence of a reactive solvent.

The results presented demonstrate that there is a need to monitor the ozonolysis products in order to determine the end-point of the reaction and to understand the range of products produced. Monitoring the reaction by GC-FID and SEC-RI provides useful complimentary information on low and high MW products although this strategy alone does not readily elucidate the mass balance of the process due to the complexity of the products and reaction sequences. In the presence of alcohols, beyond the critical time when the complete loss of carbon–carbon double bonds has been reached due to ozonolysis, a strongly exothermic reaction coinciding with the observation of rapid acid formation and aldehyde loss in GC-FID experiments was observed.

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