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Revalorization of Grape Seed Oil for Innovative Non-Food Applications

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Abstract

Grape processing produces a substantial amount of residues that are highly polluting and expensive to treat, being grape seed one of the main by-products with high commercial interest. During the extraction process of grape seed oil, most of the nutraceutical compounds remain on the solid cake. This book chapter resumes the potential utilization of grape seed oil for producing biobased materials through environmentally friendly processes that could substitute petroleum-derived products. Special attention is given to transesterification and epoxidation processes. The transesterification of grape seed oil in presence of methanol drives to the production of a biodiesel with excellent low-temperature properties. According to EN 14214, grape seed oil-based biodiesel presents a slightly lower cetane number than the specified limit. In addition, this biodiesel presents a low oxidation stability which can be improved by the incorporation of oxidation stabilizer. Attending to the epoxidation of grape seed oil, short reaction times and high temperatures are advised. Epoxidized grape seed oil can be used for the synthesis of biobased polyols and its further application on the synthesis of polyurethane compounds.

Keywords: biodiesel, biopolyol, epoxidation, grape seed oil, polyurethane foam, transesterification

1. Introduction

Grapes and grape-related products are among one of the most important horticultural products and therefore they are of high commercial interest. According to the Food and Agriculture Organization of the United Nations (FAO), the grape farming occupies 7.12 million hectares and approximately 74.49 million tonnes were produced in 2014. The top five countries

producer of grapes are China (12.6 Mton), USA (7.15 Mton), Italy (6.93 Mton), Spain (6.22 Mton), and France (6.17 Mton) [1]. Despite grapes can be commercialized as fresh fruit, dried (raisins) and in the form of jellies and jams, beverages (wine and juice) are the most important derived products. As an estimation performed by the International Organization of Vine and Wine (OIV), 276 million hL were globally produced in 2015.

The socioeconomic activity of grape pressing for producing grape juice and wine imply the generation of a considerable amount of solid wastes, since approximately 30% (w/w) of the material used become a waste. There are several environmental problems associated with wineries, including water pollution, soil degradation, damage to natural vegetation, odors, and air emissions [2].

The main solid by-products and residues produced during wine production are vine shoots, grape marc or pomace (composed by skins, seeds, and stems), and wine lees.

- Vine shoots are a non-wood lignocellulosic residue generated during the vine pruning. Manzone et al. [3] quantified the pruning residue between 1850 and 5360 kg/ha, depending on the weather conditions during the year and the structure of plantation. This residue, which is mainly composed by cellulose (34%), hemicelluloses (19%), and lignin (27%), have been used for the extraction of phenolic acids [4], lactic acid [5], and also for production of biosurfactants [6] and energy [7, 8].
- Grape marc is the main by-product of the wine industry. It is composed by stems, skins, and seeds that remains after pressing the grapes. Taking into account that the marc represents 15–20% of grapes' weight [9], around 13.03 Mt of grape marc are produced annually. The main chemical components of grape marc are phenols, which confer a high antioxidant capacity, peptic substances, cellulose, and lignin [10].
 - Grape skins can represent up to 20% of grape pomace. This winery by-product was mainly used as compost or fuel as unusable waste, overall on the small wineries. However, grape skin represents nowadays a valuable source of biologically active phytochemicals due to the high amount of phenolic compounds that contents [11].
 - Grape stems are the structure of grape bunch and represent around 3% of grape marc mass. These are composed mainly of cellulose (30.3%), hemicelluloses (21.0%), lignin (17.4%), tannins (15.9%), and proteins (6.1%). However, the compounds that can be found in grape stems depend on several factors, such as geographic origin, time of harvest, and climatic conditions [12].
 - Grape seeds are one of the main by-products from grape processing industries. An individual grape berry typically contains two/three seeds and it constitutes around 4% of grape marc. Grape seeds contain 13–19% oil, which is rich in essential fatty acids, about 11% protein, 60–70% of non-digestible carbohydrates, non-phenolic antioxidants, such as tocopherols and beta-carotene [10], and also phenolic compounds with antioxidant capacity [13].
- Wine lees, which are generated during the fermentation and aging processes of the wine, are defined as the residue formed at the bottom of recipients containing wine, after

fermentation, during storage or after authorized treatments, as well as the residue obtained by the filtration or centrifugation of this product. The lees consists of a solid phase, mainly composed by microorganisms (yeast and bacteria), insoluble carbohydrates from the cellulosic and hemicellulosic fractions, phenolic compounds, lignin, proteins and tartrates; and a liquid phase rich in ethanol, lactic acid and acetic acid [9].

The legislative situation in Europe governing the by-products produced by the wine industries only indicates that wine lees have to be withdrawn once they have been denatured to make their use in winemaking impossible. Producers with a capacity of less than 25 hL/year of wine may be exempted by the Member State from this obligation. However, most of the Member States have specified the rules for the withdrawal and legal destinations of winery industries by-products [14].

1.1. Grape seed oil

As it was previously commented, grape seed is one of the main by-products of winery industries. Even some investigations have focused on the use of grape seeds as a fuel via pyrolysis [15, 16] or gasification [17] processes, the most interesting activity from an economic point of view consists on the extraction of the interesting compounds prior to the thermal exploitation.

Grape seed oil composition has been studied by different authors, focusing mainly on the fatty acid profile, the phytochemical composition, and antioxidant properties. **Table 1** shows the fatty acid profile for grape seed oil found on a previous study [18]. These values agree with the ones found in literature. For example, Beveridge et al. [19] compared 8 different grape seed oils obtained by two different extraction methods, finding a linoleic acid content between 66.76 and 73.23%. They also reported oleic acid, palmitic acid, and stearic acids as main fatty acids in the range of 12.63–18.95%, 6.28–8.62%, 3.60–5.26%, respectively. However, slight differences on the fatty acid profile can be found due to the use of different grapes varieties and/or extraction methods [20–23].

Fatty acid		Percentage (wt.%)
Palmitic	C16:0	6.9
Palmitoleic	C16:1	0.1
Stearic	C18:0	4.0
Oleic	C18:1	19.0
Linoleic	C18:2	69.1
Arachidic	C20:0	0.3
Gadoleic	C20:1	0.3
Others		0.3

Table 1. Fatty acid composition (wt.%) of grape seed oil.

With respect to vitamin E active compounds, most of the vegetable oils only contain a significant content of tocopherols, meanwhile tocotrienols are seldom. Virgin grape seed oil contains up to 10 mg α -tocopherol/100 g and different tocotrienols with a total amount of around 35 mg/100 g [24]. Crews et al. [25] investigated the total content of tocopherols and tocotrienols of 30 samples of grape seed oil, finding a total content between 63 and 1208 mg/kg. This range is much wider than the values given at the Codex Alimentarius (240–410 mg/kg). Hassanein and Abedel-Razek [26] reported a value of 380 mg/kg of total tocopherol content. These values are relatively low compared with other vegetable oils, indicating that most of vitamin E active compounds remain on the solid phase of the seed (grape seed flour).

Phytosterols are natural sterols which occur in plants and vegetable oils. A content of phytosterols ranged from 2580 to 11,250 mg/kg phytosterols have been reported in literature. However, independently of the author, β -sitosterol is the main phytosterol found in grape seed oil (67–70%) [25, 26].

Different techniques have been proposed for grape seed oil extraction. The traditional method consists of pressing the whole seeds in a hydraulic press or the milled and heated seeds in screw press. Cold-pressing is a method of oil extraction that involves no heat or chemical treatment, and hence might retain more health beneficial components, such as natural antioxidants. The cold-pressed oils may be a better source of beneficial components, such as antioxidative phenolic compounds, as well as other health-beneficial phytochemicals. Although the yield is usually lower than that with conventional solvent extraction, there is no concern about solvent residues in the oil, making for a safer and more consumer-desired product [27]. Using this technique, Lutterodt et al. [20] determined no significant differences on the fatty acid profile of cold-pressed grape seed oil, but an increment on the oxidative stability index, indicating a higher content of antioxidant compounds.

Solvent extraction of grape seed oil is a diffusion process achieved by immersing the seed in solvent or by percolating solvent through a bed of seeds. Solvent is recovered from the oil-solvent mixture (known as micella) by an evaporator and recycled to the process. In order to determine the influence of the solvent, Fernández et al. [28] compared hexane, acetone, pentane, acetonitrile, diethyl ether, methanol, and ethanol. Among them, diethyl ether showed the highest extraction yield (20.8%). However, its use was rejected due to its high flammability and hexane was chosen as an extraction agent. It was also found that the use of polar solvents enhanced the oxidation stability of the extracted grape seed oil, indicating a higher antioxidant content in those cases. In order to combine both effects, solvents mixtures were tested and it was observed a maximum in oil yield (18.5%) and oxidation stability (16.3 h) by using a mixture hexane/acetone 1:1 (v/v). Moreover, Soxhlet and Soxtherm extraction technologies were compared, without observing a significant difference on the extraction yield nor on the oxidation stability of the oil. Luque-Rodríguez et al. [29] compared superheated hexane extraction with conventional Soxhlet system, finding that similar yields can be obtained in shorter extraction times.

Supercritical fluid extraction of vegetable oils has been intensively studied in the last decades and the results of the research are protected by several patents. However, this procedure is not applied in large-scale plants because of the difficulties with continuous

transport of seeds into, through and out of the high-pressure extractor. Smaller amounts of seeds can be extracted in semi-batch mode, with the supercritical fluid flowing through a fixed bed of material [30]. Molero Gómez et al. [31] compared the supercritical extraction and the non-supercritical one using CO₂ as extraction agent, showing a great increment on oil yield by working at supercritical conditions. Jokić et al. [32] determined that the optimal conditions for obtaining the highest oil yield (14.49%) and antioxidant activity using supercritical CO₂ as extracting agent were 400 bar and 41°C. Fiori [33] determined a break-even value of grape seed oil obtained at 550 bar and 60°C of 5.9 €/kg using the same technology. Freitas et al. [23] pointed that supercritical propane is a more suitable solvent for grape seed oil extraction since a higher extraction yield and faster kinetic was observed. However, most of authors conclude that the grape variety, the harvesting conditions, and the cultivation structure have a major influence on the grape seed oil yield, composition and antioxidant components concentration [19].

As a result of the fatty acid profile of grape seed oil with a high content of linoleic acid and the low amount of nutraceutical compounds compared with other vegetable oils, grape seed oil is not as important as olive or rapeseed oil. Moreover, phenolic compounds, whose concentration is very high in the grape seed, are only extracted into the oil only to a very small extent [24]. From this, it can be drawn that grape seed oil is not as an interesting vegetable oil as others from a nutritional point of view. Hence, in this chapter, the major non-food applications of grape seed oil are discussed, mainly focusing on the transesterification to produce biodiesel and the epoxidation and further ring-opening reactions to produce biobased polyols.

2. Transesterification of grape seed oil for biodiesel production

Biodiesel is an alternative fuel for diesel engines which is made from renewable resources, such as vegetable oils and animal fats. It is biodegradable, nontoxic, sulfur- and benzene-free and, therefore, is environmentally advantageous. The recent concern about the increase in the crude oil price, the limited resources of fossil oil, and the environmental concerns have increased the interest on vegetable oils to make biodiesel [34].

Different alternatives have been proposed on literature to increase the content of vegetable oil-based compounds on diesel fuels. The first approach consisted on directly using vegetable oils without any chemical transformation as direct fuel. Thus, soybean oil [35], sunflower oil [36], canola oil [37] or rapeseed oil [38] have been studied. However, the direct use of vegetable oils or the use of blends with traditional petroleum-based diesel has not been considered a suitable solution due to the high viscosity, the gum formation due to oxidation processes and the deposition of carbon on piston and head of the engines [39]. As an alternative, some authors proposed the pyrolysis of rapeseed oil [40], soybean oil [41] and safflower oil [42] to yield small molecules. Nevertheless, the required equipment is expensive and the obtained results do not justify the use of this technology. In addition, the pyrolysis of vegetable oils implies the remove of oxygen from biofuel, which nowadays is a legal requirement in bio-based fuels [43]. Therefore, the most interesting route to produce biodiesel from vegetable oils is the transesterification.

Transesterification reactions consists of the alcoholysis of a triglyceride to form esters and glycerol. To improve the reaction rate and yield, a catalyst is usually used. As the reaction is limited by an equilibrium, excess of alcohol is used to enhance the production of esters. Among the alcohols that can be used during the transesterification process, methanol and ethanol are the most efficient and commonly used ones. With respect to catalysts, alkalis (NaOH, KOH, carbonates, and alkoxides), acids (sulfuric acid, sulfonic acid, and hydrochloric acid), and enzymes (lipases) have been proposed in literature [44]. However, alkali-catalyzed transesterification is much faster and economically viable and, therefore, is the most often used industrial system for producing biodiesel from vegetable oils [34]. However, for alkali-catalyzed transesterification, the glycerides and alcohol must be substantially anhydrous, because water causes a partial reaction change to saponification which produces soaps. Soaps consume the catalyst and reduce the catalytic efficiency, as well as causing an increase in viscosity, the formation of gels and difficulty in achieving separation of glycerol at the end of the reaction [44].

In respect to the transesterification mechanism, it consists of three consecutive reversible reactions where the triglyceride is converted into diglyceride, monoglyceride, and finally, glycerol, liberating a mole of esters at each step (**Figure 1**). After the transesterification reaction, a mixture of esters, glycerol, alcohol, catalyst, and unreacted tri-, di-, and monoglycerides is obtained.

The obtained transesterification product should be purified and characterized to quantify the global biodiesel quality. **Table 2** shows the requirements of the most important regional standards and the analytic methods.

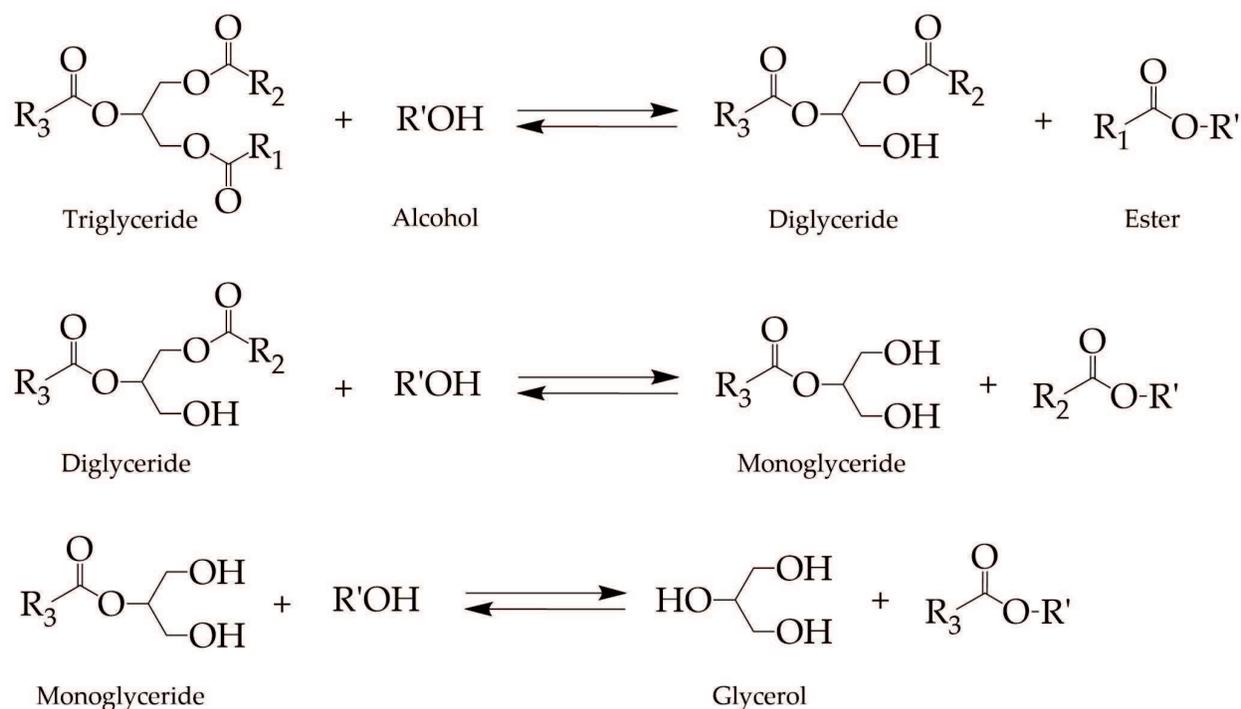


Figure 1. The transesterification reaction of triglycerides with alcohol.

Parameter	Units	EU (EN 14214:2012)		USA (ASTM D6751-15ce1)	
		Limit	Method	Limit	Method
Ester content	% (m/m)	>96.5	EN 14103	—	—
Density at 15°C	kg/m ³	860–900	EN ISO 3675 EN ISO 12185	—	—
Viscosity at 40°C	mm ² /s	3.50–5.00	EN ISO 3104	1.9–6.0	ASTM D445
Flash point	°C	>101	EN ISO 2719 EN ISO 3679	>93	ASTM D93
Distillation temperature (90% recovered)	°C	—	—	<360	ASTM D1160
Cetane number	—	>51.0	EN ISO 5165	>47	ASTM D613
Copper band corrosion	Classification	1	EN ISO 2160	3	ASTM D130
Oxidation stability	h	>8.0	EN 14112 EN 15751	>3.0	EN 15751
Acid value	mg KOH/g	<0.50	EN 14104	<0.50	ASTM D664
Iodine value	g I/100 g	<120	EN 14111 EN 16300	—	—
Cloud point	°C	*	EN 23015	Report	ASTM D2500
CFFP	°C	*	EN 116	—	—
Methyl linoleate	% (m/m)	<12.0	EN 14103	—	—
Polyunsaturated methyl esters	% (m/m)	<1.00	EN 15779	—	—
Methanol content	% (m/m)	<0.2	EN 14110	<0.2	EN 14110
Monoglyceride content	% (m/m)	<0.70	EN 14105	<0.40	ASTM D6584
Diglyceride content	% (m/m)	<0.20	EN 14105	—	—
Triglyceride content	% (m/m)	<0.20	EN 14105	—	—
Free glycerol	% (m/m)	<0.02	EN 14105 EN 14106	<0.02	ASTM D6584
Total glycerol	% (m/m)	<0.25	EN 14105	≤0.24	ASTM D6584
Water content	mg/kg	<500	EN ISO 12937	—	—
Carbon residue	% (m/m)	—	—	<0.05	ASTM D4530
Water and sediment	% vol.	—	—	<0.05	ASTM D2709
Total contamination	mg/kg	<24	EN 12662	—	—
Sulphated ash content	% (m/m)	<0.02	ISO 3987	<0.02	ASTM D874
Sulfur content	mg/kg	<10.0	EN ISO 20846 EN ISO 20884 EN ISO 13032	<15	ASTM D5453

Parameter	Units	EU (EN 14214:2012)		USA (ASTM D6751-15ce1)	
		Limit	Method	Limit	Method
Cold soak filterability test	s	—	—	<200	ASTM 7501
Group I metals (Na + K)	mg/kg	<5.0	EN 14108 EN 14109 EN 14538	<5.0	EN 14538
Group II metals (Ca + Mg)	mg/kg	<5.0	EN 14538	<5.0	EN 14538
Phosphorous content	mg/kg	<4.0	EN 14107 EN 16294	<10	ASTM D4951

*Differences exist between the national versions of the EN 14214 standard. These differences relate to cold weather requirements and are detailed in the national annex of each standard.

Table 2. Comparison of the European and American biodiesel quality standards.

Among the general parameters for biodiesel, the viscosity controls the characteristics of the injection into the engine. The viscosity of fatty acid methyl esters can reach very high values when the vegetable oil used as raw material is highly unsaturated and, therefore, it should be controlled. The flash point of a fuel is the temperature at which it will ignite when exposed to a flame or a spark. The flash point of biodiesel is higher than the petroleum-based diesel, which is safe for transport purposes. Cetane number measures how easily ignition occurs and the smoothness of combustion. Cetane number is a critical variable because it affects important performance parameters such as combustion, stability, production of white smokes, noise, and emissions of CO and hydrocarbons. The presence of mono-, di-, and triglycerides, and other non-interesting products (alcohol, glycerol, phosphorylated and sulfated compounds, etc.) cause engine problems, such as fuel filter plugging, carbon deposition, and hydrolytic and oxidative reactions of fatty acid methyl esters [34].

In their previous work, Ramos et al. [18] studied the influence of vegetable oils properties and composition on the quality of biodiesel synthesized from different vegetable oils. Among them, grape seed oil was also used as raw material. As a resume, **Table 3** shows a comparison of properties of biodiesel obtained using different vegetable oils.

As can be observed, grape seed oil-based biodiesel shows similar values of ester content, viscosity, flash point, and acid value to those obtained from traditional vegetable oils (soybean oil, sunflower oil, etc.). However, iodine number, cetane number, and oxidative stability exclude the direct use of this biodiesel because their values are out of the range indicated by the major biodiesel standards.

Iodine number is an important parameter on biodiesel quality, since heating highly unsaturated fatty acid methyl esters results in polymerization. This can lead to the formation of deposits or to deterioration of the lubricant properties of biodiesel. It is well known that biodiesel cetane number depends on the feedstock used for its production. The longer and the more saturated the fatty acid carbon chains, the higher the cetane number [45]. Also,

Parameter	Grape	Palm	Olive	Rape	Soybean	Sunflower
Ester content (% mass)	97.8	97.7	99.0	99.5	96.9	97.2
Viscosity at 40°C (mm ² /s)	4.1	4.5	4.5	4.4	4.2	4.2
Flash point (°C)	175	176	178	170	171	177
Cetane number	48	61	57	55	49	50
Oxidative stability at 110°C (h)	0.5	4.0	3.3	2.0	1.3	0.8
Acid value (mg KOH/g)	0.27	0.12	0.13	0.16	0.14	0.15
Iodine value (g I/100 g)	138	57	84	109	128	132
Linoleic acid content (% mass)	0.4	0.2	0.6	7.9	6.3	0.2
CFPP (°C)	-6	10	-6	-10	-5	-3
Methanol content (% mass)	0.00	0.00	0.00	0.00	0.00	0.00
Monoglyceride content (% mass)	0.28	0.17	0.67	0.41	0.21	0.37
Diglyceride content (% mass)	0.08	0.06	0.09	0.08	0.10	0.07
Triglyceride content (% mass)	0.03	0.04	0.03	0.03	0.07	0.04
Free glycerol (% mass)	0.00	0.01	0.00	0.01	0.07	0.00
Total glycerol (% mass)	0.09	0.06	0.19	0.09	0.00	0.11

Table 3. Properties of biodiesel obtained from different vegetable oils via transesterification.

oxidation stability is one of the major issues affecting the use of biodiesel because it is very difficult to meet the 6 h of stability required by most of the main standards, even for many common raw materials. Therefore, since linoleic acid (C18:2) is the majoritarian fatty acid on grape seed oil composition, cetane number, iodine value, and oxidation stability requirements cannot be easily accomplished.

On the other hand, biodiesel obtained from grape seed oil showed some excellent properties, such as a very low cold filter plugging point (CFPP). Certain types of biodiesel present an operability problem based on the wax settling and plugging of filters and fuel lines when overnight temperatures approach. Low-temperature properties depend mostly on the saturated ester content. In this sense, grape seed oil barely contains a 11% of saturated fatty acid methyl esters, so its excellent CFPP is justified [46, 47].

To improve the performance of grape seed oil as biodiesel feedstock, different approaches have been discussed in literature. One of the most common solutions consists of the biodiesel-biodiesel blending from different feedstocks. Fernández et al. [28] studied the feasibility of blending jatropha, grape, rape and palm biodiesel, finding good properties at specific mixing portions. Atabani et al. [48] improved the kinematic viscosity of *Sterculia foetida* methyl esters by blending it with soybean-based biodiesel. Also, biodiesel has been blended with petroleum-based diesel and other fuels to meet the standards requirements [49, 50].

The issue of oxidative stability affects biodiesel mainly during extended storage. Generally, factors such as presence of air, elevated temperatures or presence of metals facilitate oxidation. Several approaches have been discussed in literature to either prevent or decelerate oxidation rate [51, 52]. The most obvious solution consists on preventing contact of the biodiesel with atmospheric air. Another solution is to prevent contact with prooxidative substances and avoid elevated temperatures and light. However, these solutions are not always viable and the use of antioxidants is of significant interest. Different natural and synthetic antioxidants had been used on biodiesel obtained from different vegetable oils. The most interesting result, apart from the obvious increment on oxidative stability, was that properties such as viscosity, CFPP, density, carbon residue and sulphated ash remained constant [53]. Different antioxidants, such as vitamin E [54], tocopherols [55], and synthetic ones (butylated hydroxytoluene, tert-butyl hydroquinone, and pyrogallol) [56], had been studied over biodiesel obtained from different feedstocks.

Nevertheless, grape seed oil-based biodiesel has been used for different applications. For example, Karthikeyan [57] proposed its use as a biofuel in marine engines by blending it with traditional petroleum-based fuel. It was found that flash point, cloud point and pour point were improved and NO_x emissions were significantly reduced. Bazooyar et al. [58] compared the behavior of biodiesels based on various vegetable oils in a semi-industrial boiler. Grape seed oil biodiesel showed the lowest CO and CO₂ emissions. Hence, it can be concluded that grape seed oil can be used.

3. Epoxidation of grape seed oil

Epoxidation reaction consists of the addition of an oxygen atom to a carbon-carbon double bond. This reaction has been established as one of the most important methods for the formation of carbon-oxygen bonds [59]. Epoxides are highly reactive and versatile functional groups which are commonly used as precursors for alcohols, glycols, carbonyls, alkanolamines, substituted olefins, polyester polyurethanes, and epoxy resins [60, 61]. Increasing environmental problems related to fossil sources overuse have made plant oils an attractive alternative for the production of epoxy-based materials.

In the industry, epoxidized vegetable oil, and more specifically soybean and linseed oil, are currently used as plasticizers for PVC and related resins, reaching an annual production of about 200,000 tons [62]. Indeed, the epoxides change the solubility and flexibility of the PVC resins and react with hydrochloric acid liberated from the PVC resins under the prolonged action of light and heat. Epoxidized vegetable oils are also used as lubricants [63, 64] and as prepolymer in coating formulations [65–67]. The applicability of an epoxidized oil depends on its purity, oxirane number, and iodine number.

There are three different potential sources of vegetable oils containing epoxy groups. Firstly, there is a variety of natural occurring epoxy vegetable oil, mainly *Vernonia galamensis* [68] and *Euphorbia lagascae* oil [69], which contain up to 70% of vernolic acid (12S,13R-epoxy-9-cis-octadecenoic acid). The second option consists of the production of oil from genetically modified seeds which already contains vernolic acid in order to increase its content [70, 71].

However, none of these vegetable oils are commercially available at a competitive cost. Therefore, the only remaining solution is the chemical transformation of unsaturated vegetable oils, such as soybean [72] or grape seed oil [73], into epoxidized vegetable oils.

A wide variety of methods have been proposed for epoxidation of vegetable oils and related products (e.g., unsaturated free fatty acids). The most important ones are listed below [74]:

- Chlorohydrin process: this indirect epoxidation process is based on the reaction of the unsaturation with HOCl, forming the chlorohydrin which subsequently yields the epoxide on alkaline treatment. However, this method is highly unfriendly environmentally.
- Halcon reaction: epoxides can also be prepared by treating the unsaturations with tert-butyl hydroperoxide using vanadium, titanium or molybdenum complexes as catalysts.
- Epoxidation with dioxirane: the enantioselective epoxidation in a neutral medium is made possible by using dioxirane and an optically active manganese (III) salt as catalyst.
- Epoxidation with molecular oxygen: this process is catalyzed by silver and is the cheapest and greenest route to epoxidize low molecular weight molecules (e.g., ethylene and butadiene). However, this process is not efficient to be applied to vegetable oils, but its use is mostly restricted to low molecular weight substrates.

However, the selectivity and workup of these processes are not satisfactory for industrial applications, and currently, the industrial processes are based on the use of peracids. The Prilezhaev reaction consists on the epoxidation of alkenes with peracids, typically performic or peracetic acid, formed *in situ* from hydrogen peroxide and formic or acetic acid, respectively. Among them, peracetic acid is the most used one due to its low price, higher epoxidation efficiency, and safety issues at ordinary temperatures. Acidic catalysts, either strong acids or acidic ion exchange resins, are required on this process. Dinda et al. [75] found that the order of catalyst effectiveness for the vegetable oil epoxidation reaction based on mineral acids was headed by H_2SO_4 , followed by H_3PO_4 , HNO_3 , and HCl.

During the *in situ* epoxidation process, different reactions take place. Firstly, the peracid must be formed from hydrogen peroxide and the carboxylic acid. Secondly, the previously formed peracid attacks the alkene group, generating an oxirane group and the carboxylic acid. Hence, the carboxylic acid is not consumed during the epoxidation reaction. However, two side reactions might take place during the epoxidation process. Since oxirane rings are formed in aqueous acidic media, they can be hydrolysed into hydroxyl groups. Consequently, reactions between hydroxyl groups form different triglycerides leading to the formation of oligomers linked by ether groups.

3.1. A case study: influence of temperature on grape seed oil epoxidation

Grape seed oil was epoxidized using peracetic acid formed *in situ* from acetic acid and hydrogen peroxide using H_2SO_4 as catalyst. The epoxidation reactions were carried out at 50, 60, 90, and 100°C [73]. To evaluate the conversion and selectivity of the process, the concentration of different functional groups was determined.

Figure 2 shows the evolution of double bonds, epoxy groups, and hydroxyl groups along the reaction time at the previously commented reaction temperatures.

As can be observed, a gap exists in the double bond conversion (**Figure 2A**), depending on the reaction temperature, with increased conversion at greater temperature. If the temperature is higher than 90°C, conversions greater than 90% can be obtained in less than 1.5 h. Complete conversion of double bonds was only achieved when the reaction temperature and time were 100°C and 4 h, respectively. However, the double bonds conversion decreased much slower when the reaction temperature was 60°C or lower, requiring reaction times longer than 6 h for complete double bond conversion. Nevertheless, high double bond conversion rate cannot be the desired reaction conditions because the presence of secondary reactions can be promoted.

In respect to the oxirane ring formation (**Figure 2B**), the obtained data also indicated an important influence of reaction temperature. The reactions performed at high temperature (90 and 100°C) showed a maximum concentration of epoxide groups at short reaction times, between 1 and 1.5 h. After this, oxirane rings were completely consumed when the reaction time was 6 h. However, when the reaction was performed at lower temperatures (50 and 60°C), the epoxide group concentration increased constantly during the reaction, without observing any depletion.

In the same way, the hydroxyl group concentration (**Figure 2C**) increased abruptly at 100°C, reaching its maximum value in 4 h. At this point, the hydroxyl group concentration decreased in the reaction media, indicating the presence of another secondary reaction. On the other hand, when the reaction was performed at lower temperatures, the hydroxyl group formation was almost negligible.

The diminishing in the concentration of hydroxyl groups at 100°C indicates the presence of another secondary reaction, which mainly takes place when oxirane rings exist. The most common reaction in these cases reported in literature consists of the oligomerization of triglycerides. The generation of oligomers in the reaction bulk was confirmed by Gel Permeation Chromatography (GPC). All chromatograms presented three peaks, indicating the presence of dimers and trimers in addition to the main product.

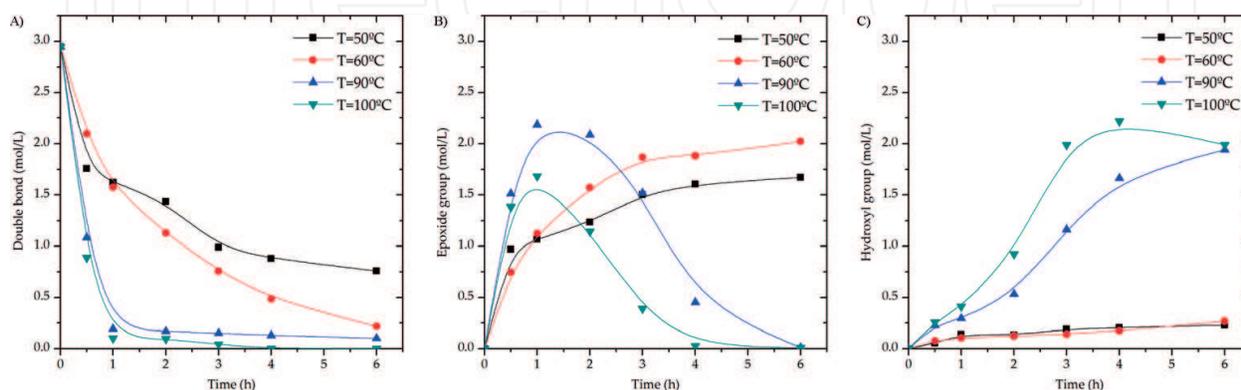


Figure 2. Concentration of different functional groups along the reaction time as function of different temperature used.

The concentration of oligomers (dimers and trimers) could be calculated through the mass balance presented in Eq. (1). This mass balance indicates that the initial content of double bonds ($DB_{t=0}$) is equal to the unreacted double bonds (DB_t), the oxirane rings (OR_t), half of the hydroxyl groups (OH_t), and the oligomers ($OLIG_t$). The portion of dimers (DIM) and trimers (TRIM) was quantified using the area ratio of these compounds from the chromatograms. In this estimation, the same response factor was assumed for both dimers and trimers. The obtained values are presented in **Figure 3**.

$$DB_{t=0} = DB_t + OR_t + \frac{OH_t}{2} + OLIG_t \quad (1)$$

When the epoxidation reaction was performed at low temperature (50 or 60°C), oligomer formation was almost neglected. However, the oligomer concentration profiles obtained at high temperatures (90 and 100°C) indicate that the formation of dimers (**Figure 3A**) is required to form a trimer (**Figure 3B**) and that a unique reaction step is not taken place. Moreover, a change in the trend can be observed at a reaction time of 1.5 and 2.5 h for the reactions performed at 90 and 100°C, respectively. This result could be explained by the lack of oxirane ring groups in the reactor at this time, suggesting that the formation of oligomers requires the presence of both oxirane rings and hydroxyl groups.

3.2. Kinetic model for the *in situ* epoxidation of grape seed oil

Janković and Sinadinović-Fišer [76] have already postulated a kinetic model for the *in situ* formation of peracetic acid from acetic acid and hydrogen peroxide in the presence of a homogeneous acid catalyst. The mechanism can be summarized in the following steps: (i) formation of peracetic acid in the presence of the catalyst and (ii) reaction between peracetic acid and the double bonds to produce oxirane rings, releasing acetic acid. Moreover, different secondary reactions were observed during the epoxidation of grape seed oil: the hydrolysis of oxirane

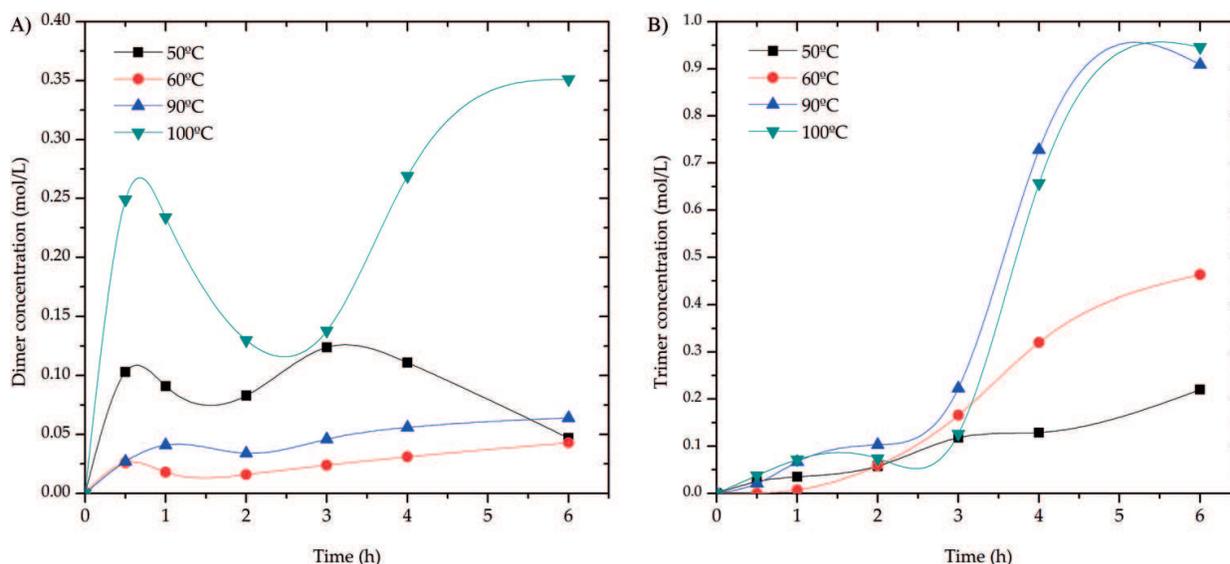


Figure 3. Concentration of dimmers and trimmers along the reaction time as a function of different temperature used.

rings (iii) and the formation and dimers (iv) and trimers (v). Finally, it is important to take into account the degradation of hydrogen peroxide in water (vi) [77].

From the above mechanism, the following reaction system (Eqs. (2)–(7)) can be proposed:



where AA, PAA, DB, OR, OH, DIM, and TRIM represent the acetic acid, peracetic acid, double bond, oxirane ring, hydroxyl groups, dimers, and trimers, respectively.

The kinetic model was simplified assuming that the epoxidation reaction takes place in a unique phase (i.e., pseudo-homogeneous system). This assumption avoids the use of distribution constants, which would be necessary to quantify the concentration of the species in the organic and aqueous phases. To minimize the error caused by this assumption on the kinetic model, a high agitation rate was used. This high agitation rate favors the formation of small oil drops in the aqueous phase, increasing the external surface for mass transfer and minimizing limitations to the mass transfer [73].

Therefore, the corresponding differential equation system (Eqs. (8)–(16)) can be drawn from the proposed reaction set:

$$\frac{d[AA]}{dt} = -k_0[AA][H_2O_2] + k_1[PAA][H_2O] + k_2[PAA][DB] \quad (8)$$

$$\frac{d[H_2O_2]}{dt} = -k_0[AA][H_2O_2] + k_1[PAA][H_2O] - k_6[H_2O_2] \quad (9)$$

$$\frac{d[PAA]}{dt} = k_0[AA][H_2O_2] - k_1[PAA][H_2O] - k_2[PAA][DB] \quad (10)$$

$$\frac{d[H_2O]}{dt} = k_0[AA][H_2O_2] - k_1[PAA][H_2O] - k_3[OR][H_2O] + k_6[H_2O_2] \quad (11)$$

$$\frac{d[DB]}{dt} = -k_2[PAA][DB] \quad (12)$$

$$\frac{d[OR]}{dt} = k_2[PAA][DB] - k_3[OR][H_2O] - k_4[OR][OH] - k_5[OR][DIM] \quad (13)$$

$$\frac{d[OH]}{dt} = 2k_3[OR][H_2O] - k_4[OR][OH] \quad (14)$$

$$\frac{d[DIM]}{dt} = k_4[OR][OH] - k_5[OR][DIM] \quad (15)$$

$$\frac{d[TRIM]}{dt} = k_5[OR][DIM] \quad (16)$$

The differential equation system was solved numerically by using the fourth-order Runge-Kutta method. Hence, all the kinetic constants (k_i) were calculated by fitting the experimental concentrations of the species to those predicted from the equations Eqs. (8)–(16).

A comparison between the experimental values and the theoretical trends for the concentration of DB, OR, OH, DIMS, and TRIMS is shown at **Figure 4**. As can be observed, a good agreement exists among the experimental and predicted values, with an error lower than

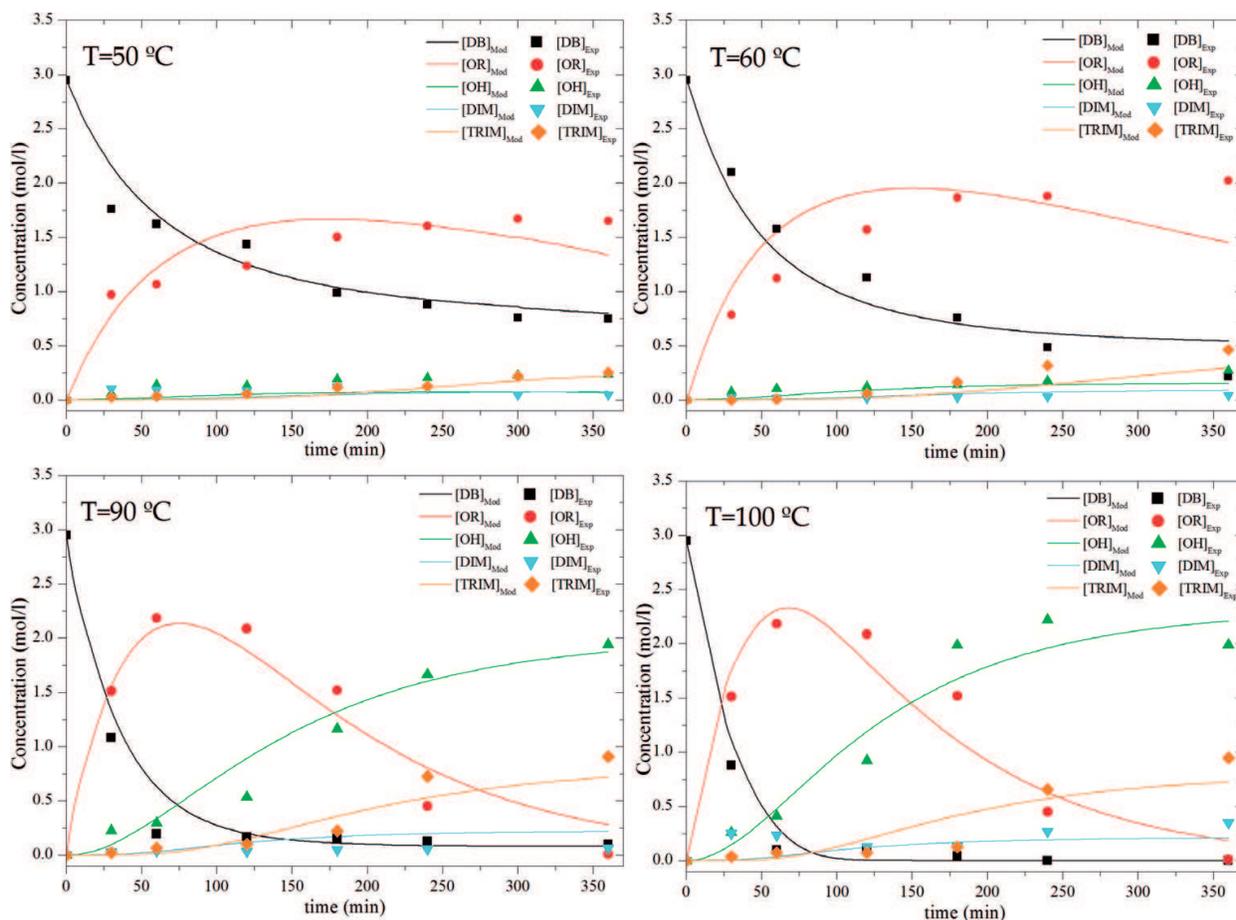


Figure 4. Theoretical and experiential profiles of functional groups along the reaction time for different temperatures.

T (°C)	k_0 (L/mol min)	k_1 (L/mol min)	k_2 (L/mol min)	k_3 (L/mol min)	k_4 (L/mol min)	k_5 (L/mol min)	k_6 (L/min)
50	1.35×10^{-2}	6.56×10^{-2}	0.129	0.247×10^{-4}	0.106×10^{-3}	1.04×10^{-2}	5.85×10^{-3}
60	1.20×10^{-2}	4.02×10^{-2}	0.178	0.288×10^{-4}	5.94×10^{-3}	1.05×10^{-2}	7.10×10^{-3}
90	1.01×10^{-2}	0.102×10^{-2}	0.485	1.38×10^{-4}	3.81×10^{-3}	1.50×10^{-2}	0.14×10^{-3}
100	0.990×10^{-2}	0.573×10^{-2}	0.560	1.75×10^{-4}	3.07×10^{-3}	1.70×10^{-2}	6.30×10^{-3}

Table 4. Kinetic constants for the proposed model.

0.5% in all cases. Student's t -test was performed, observing in all cases t values lower than the critical one (2.56) [73].

Table 4 shows the obtained values for the kinetic constants. All the kinetic constants presented the same order of magnitude, excepting k_3 , which was the lowest. This lower value could be related to the high concentration of water that was considered in this model by neglecting the presence of a secondary aqueous phase. Therefore, it is expected that this value would increase in a two-phase model. Respecting to the values of k_0 and k_1 , it indicates that the peracetic formation is not favorable at high temperatures. Moreover, the kinetic constants k_4 and k_5 indicate that the formation of trimers is favored over dimers one.

One of the most traditional representations of kinetic constants is the Arrhenius equation (Eq. (17)). To obtain the pre-exponential factor (A) and the activation energy (E_A), all obtained constants for the chemical reactions were adjusted by non-linear fitting.

$$k = A \cdot e^{\frac{-E_A}{R \cdot T}} \quad (17)$$

The E_A , A , and coefficient of determination values (R^2) are summarized in **Table 5**. A good fit between the experimental kinetic constants and the Arrhenius equation was observed for all reactions, except for the reverse reaction of peracetic acid synthesis (k_1).

Different authors have determined the E_A value of different *in situ* epoxidation system using different vegetable oils as raw materials. For example, Cai et al. [78] and Mungroo et al. [79] found a value of 10.3 and 10.7 kcal/mol, using soybean and canola oil as raw material, respectively. There is a small difference among these values and our determined one (7.3 kcal/mol). Janković and Sinadinović-Fišer [76] concluded that the number and the position of the double bonds, their position with respect to the carboxylic group, and the presence of *cis*- or *trans*-isomers have

Kinetic constant	k_0	k_1	k_2	k_3	k_4	k_5	k_6
E_A (kcal/mol)	-1.46	-16.51	7.30	10.19	-5.33	2.47	5.33
A	1.35×10^{-3}	4.35×10^{-13}	1.12×10^4	171	2.27×10^{-6}	0.468	23.18
R^2	0.972	0.738	0.994	0.979	0.937	0.966	0.996

Table 5. Arrhenius equation parameters.

a strong influence on the activation energies. Moreover, E_A values are affected by the simplifications and assumptions considered along the proposed model. Therefore, slight differences in the activation energies values are expected.

4. Synthesis of biopolyols

The uncertainty of petroleum price and its availability, combined with the global and institutional tendencies toward the principles of green chemistry, have forced the chemical industry to explore the use of renewable resources. Polyurethanes (PUs), with a global production of 12.28 Mt in 2010, are the sixth most widely used polymer [80]. This is due to the high versatility of use in mostly all the fields of polymer applications: foams, elastomers, adhesives, coatings, sealants, fibers, etc. PUs are obtained by the reaction of a polyol and a polyisocyanate, being both of these raw materials typically obtained from petroleum. However, the chemical industry is paying a great interest to the production of biobased polyols (biopolyols).

The most interesting alternative to produce biopolyols consists of the chemical transformation of unsaturated vegetable oils through different alternatives to produce hydroxyl groups, which enable the reaction with polyisocyanates to get PUs. Some of the proposed routes in literature are the ozonolysis-hydrogenation process [81], hydroformylation [82], dimerization of fatty acids [83], thiol-ene coupling [84], and formaldehyde addition [85]. However, the most used one consists of the epoxidation of double bonds and its further epoxide ring opening.

4.1. Ring-opening reaction with glycerol

To obtain desired biopolyols, the oxirane rings can be opened with compounds containing active hydrogen atoms, such as monoalcohols [86], amines [87, 88] or carboxylic acids [89], among others.

In addition, if diols or triols are used as nucleophile for epoxide ring opening, then both primary and secondary hydroxyl functions could be inserted on each epoxide group. Thus, although the production of polyols from different vegetable oils has been reported, there is a lack of information about the yield of this reaction toward hydroxyl groups and the viability of using grape seed oil as unsaturated vegetable oil.

Therefore, in this work, the ring-opening reaction was carried out using glycerol as ring-opening agent and double metal cyanide (DMC) complex as catalyst (**Figure 5**) [90].

The epoxidized grape seed oil previously produced, with an oxirane oxygen concentration of 5.87%, a hydroxyl value of 31.98 mg KOH/g, and an average molecular weight of 1151.75, was stirred at 900 rpm during 2 h at 80°C. **Figure 6** shows the infrared spectrum of the grape seed oil, the epoxidized oil, and the green-polyol obtained after ring-opening reaction with glycerol. It can be observed a drop in the intensity of the bands at 3009 and 1660 cm^{-1} related to unsaturations during the epoxidation reaction. Moreover, a big increase in the intensity area at the stretching band of 3500 cm^{-1} is observed, which confirms the rupture of the oxirane ring and the incorporation of a large number of terminal hydroxyl groups from the glycerol molecule.

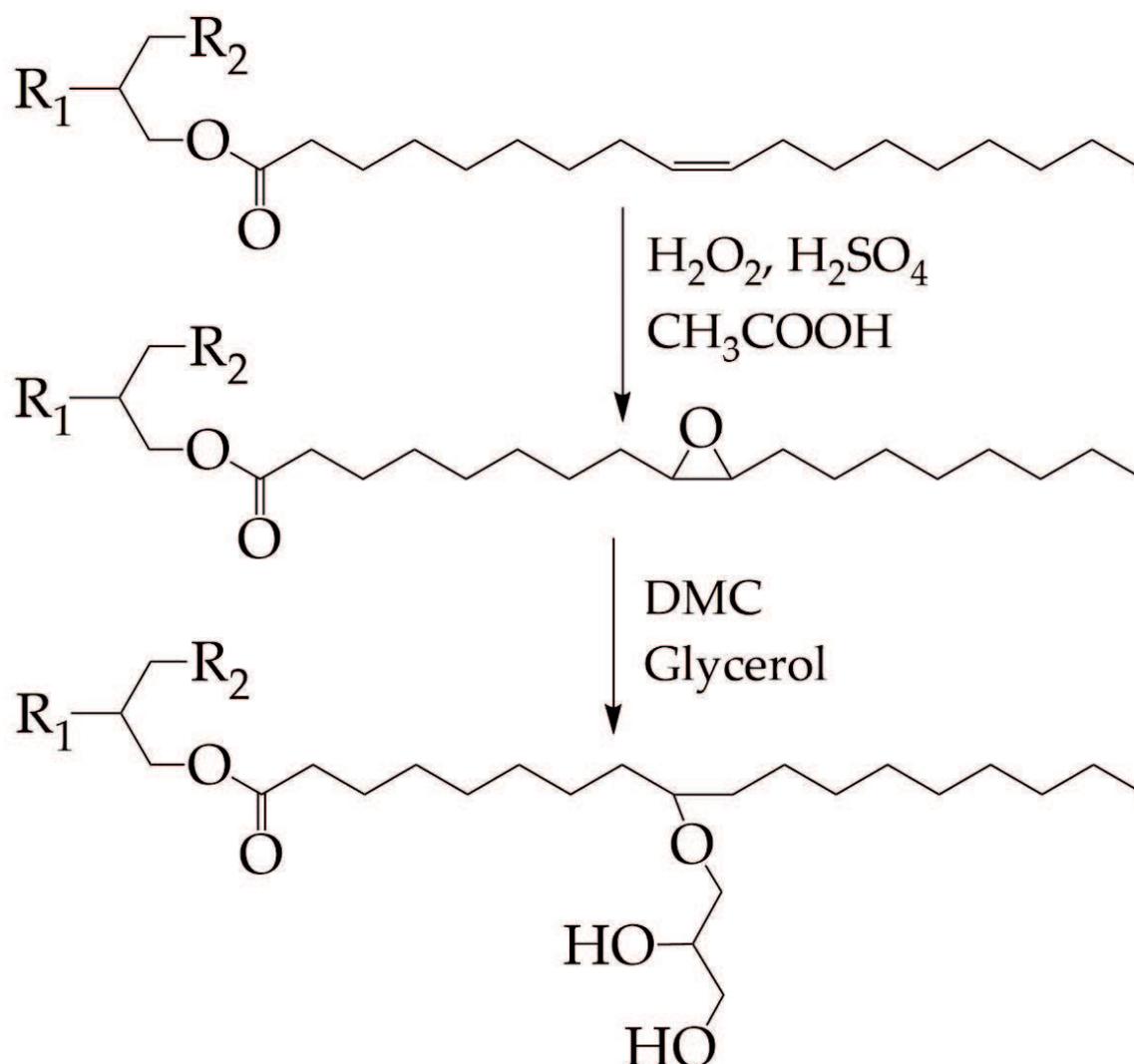


Figure 5. Reaction scheme of the ring-opening process in presence of glycerol.

The developed renewable green-polyol presents the following characteristics: an oxirane oxygen concentration of 1.06%, a hydroxyl value of 80.84 mg KOH/g, and an average molecular weight of 1800.94 g/mol. These values indicate that 82% of the oxirane rings were opened by the glycerol.

4.2. Ring-opening reaction with NaN_3

As it was previously commented, biopolyols synthesized from epoxidized vegetable oils can be functionalized by different groups, when the epoxide group is hydrolysed. Among the possible pathways, the ring-opening reaction with sodium azide [91] is one of the most interesting alternatives for obtaining very interesting compounds (**Figure 7**) [92].

The presence of nitrogen atoms in the structure of the biopolyol resulting from the incorporation of azide groups enables the polyol to act as thermal stabilizer compound in polyurethane foams [93]. Additionally, the azide group is highly polar, and when it is linked to a hydrocarbon chain, the hydrophobic character is modified, favoring its use as a surfactant [94].

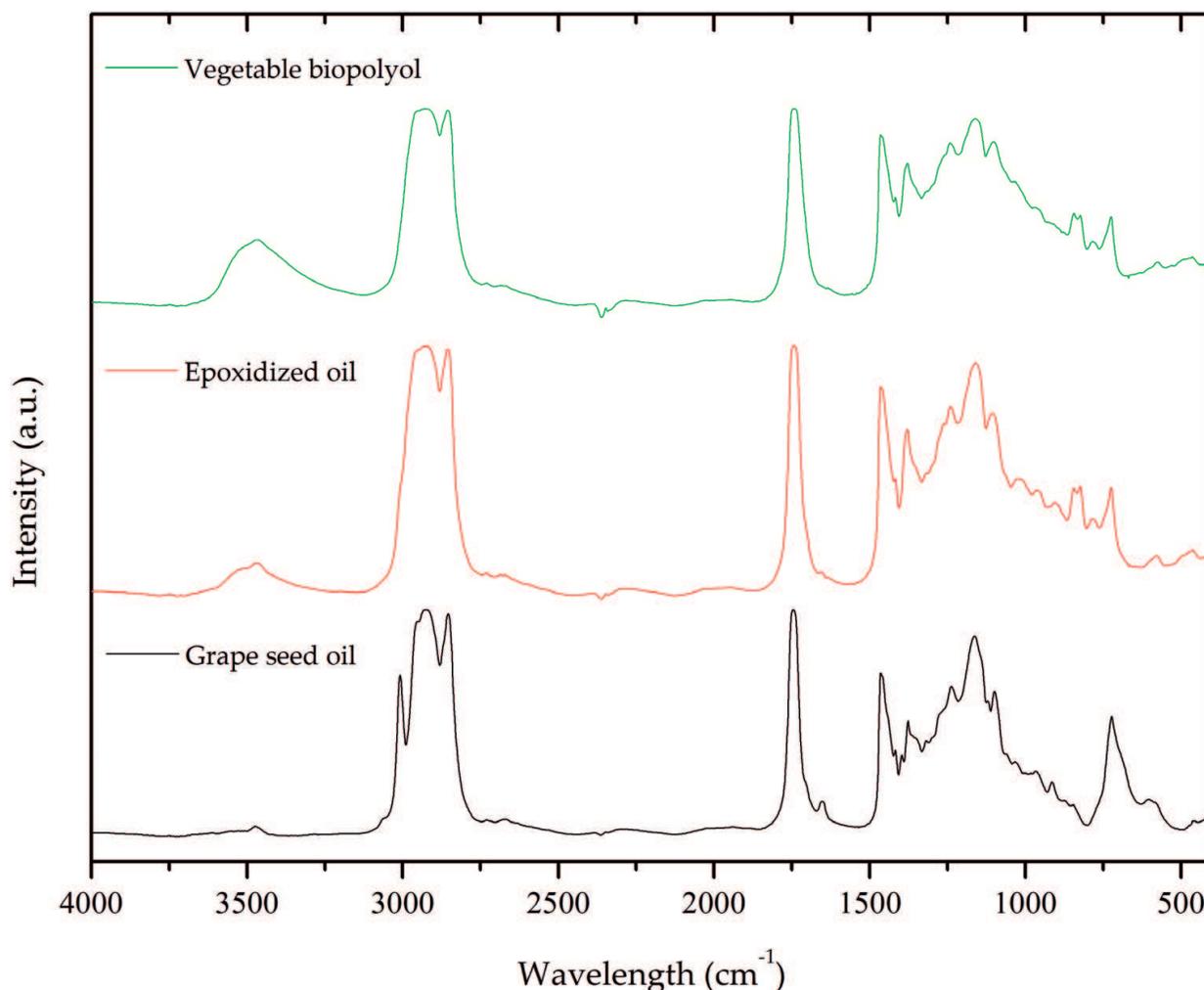


Figure 6. Infrared spectrum of the grape seed oil, the epoxidized oil, and the vegetable biopolyol.

Moreover, the azide group is one of the two main parts for performing the 1,3-dipolar cycloaddition reaction among azides and alkynes in the field of click chemistry [95]. The latter one is of the most actively investigated approaches for preparing tailor-made bioactive substances at this time.

The azidification reaction was performed at three different temperatures (50, 60, and 70°C) for 24 h. Samples were extracted at four points: 1, 2, 4, and 24 h [92]. The hydroxyl value and oxirane content of the synthesized azidified biopolyols are presented in **Figure 8**.

As can be observed, high reaction times and temperatures favor the transformation of oxirane rings into hydroxyl groups. The influence of temperature was determined considering that the reactions follow a pseudo-first-order kinetics. Hence, the observed kinetic constant (k_{obs}) can be determined from the slope of the representation $\ln(C_{epox})$ vs. reaction time. The high correlation coefficient ($R^2 = 0.990$) indicated a good fit between the experimental and theoretical values. Moreover, it is also remarkable that longer reaction times than 24 h are required to achieve full conversion of epoxide groups. However, the polyol obtained after 24 h at 70°C was used for the subsequent foaming process.

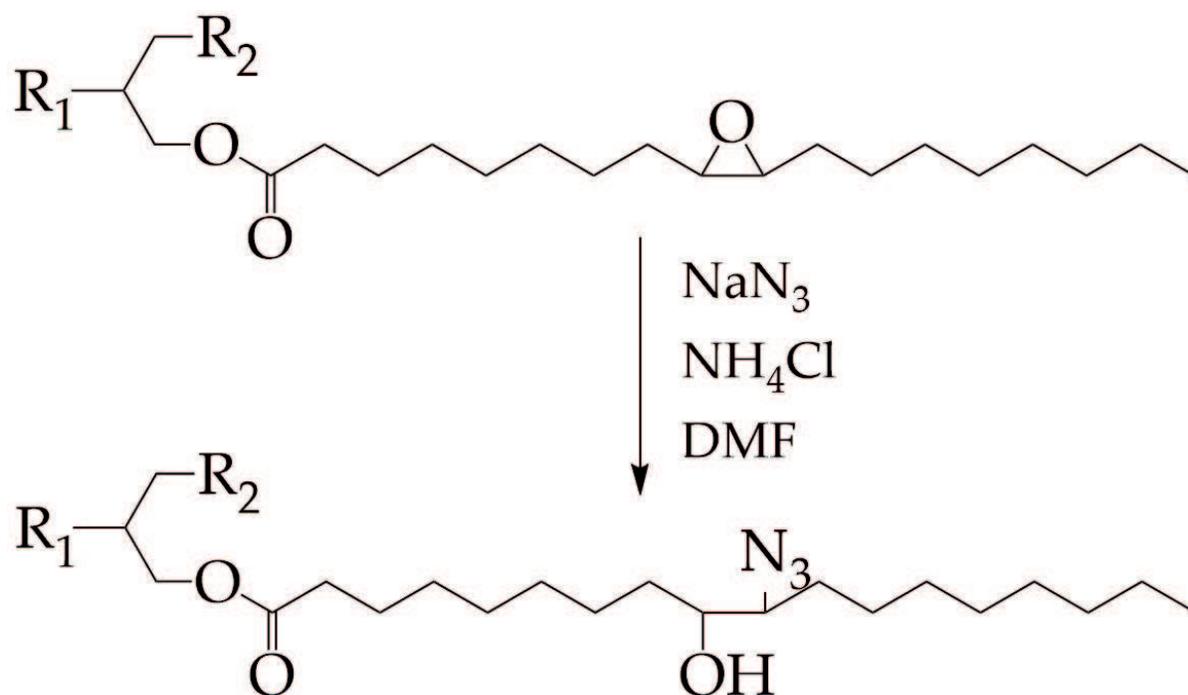


Figure 7. Reaction scheme of the ring-opening process in presence of sodium azide.

Kinetic constant values of 2.70×10^{-2} , 5.05×10^{-2} , and $7.18 \times 10^{-2} \text{ s}^{-1}$ were obtained at 50, 60, and 70°C, respectively. As expected, higher reaction temperatures favored the ring-opening reaction. Arrhenius equation (Eq. (17)) was used to determine the E_A and A for the proposed reaction system. Also in this case, a good correlation ($R^2 = 0.987$) was observed. E_A and A was calculated from the slope and y-intercept of its linearized form, obtaining values of $E_A = 0.341 \text{ J/mol}$ and $A = 0.121$.

4.3. Rigid polyurethane foam synthesis

As was stated previously, polyurethanes constitute a large family of polymers which is characterized for their versatility. Depending on the characteristics and structures of polyols and polyisocyanates, polyurethanes can be obtained as thermoplastics, adhesives, coatings, foams, etc. Rigid polyurethane foams are widely used in different applications, such as thermal [96] and acoustic [97] insulation.

The versatility of these products and the great consumption of polyurethanes (PUs) in the new emerging economies, which are believed to increase in incoming years, are forcing researchers to find alternative raw materials to avoid the petroleum dependence. Related to this, use and disposal of petroleum-based PUs is to be taken into account. Therefore, since polyol components usually are around half the weight of the final product, the use of greener polyols in PU synthesis has attracted much interest during the last decade [98].

In this section, different rigid PU foams were synthesized from the previously synthesized grape-seed-oil-based polyols. The commercial polyol Alcupol R4520 was used as a reference

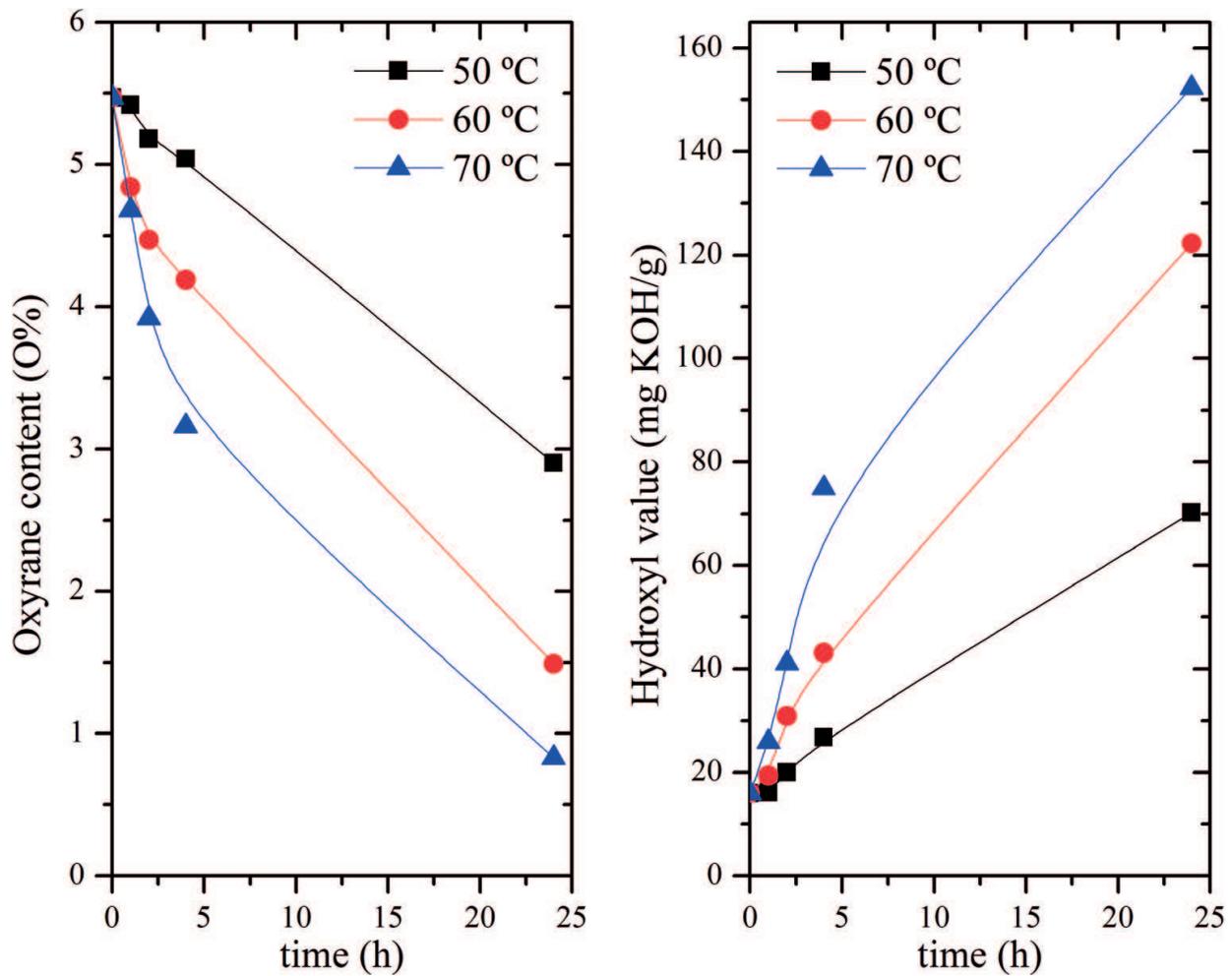


Figure 8. Oxirane content and hydroxyl values for the azidified biopolyol obtained at different reaction temperatures during 24 h.

	Foam A	Foam B	Foam C
Type of polyol	R4520	Vegetable biopolyol	Azidified biopolyol
Polyol (wt.%)	47.75	48.43	47.75
Water (wt.%)	0.75	1.21	0.75
Tegostab B8404 (wt.%)	3	0.73	3
Tegoamin 33 (wt.%)	0.37	0.37	0.37
Tegoamin BDE (wt.%)	0.37	1.20	0.37
MDI (wt.%)	47.76	48.06	47.76

Table 6. Weight percentages of raw materials for the synthesis of rigid PU foams.

material to compare the internal structure and properties of the final product. **Table 6** shows the formulations used to synthesize the PU foams. The required quantities of these reactants were calculated based on the hydroxyl number of the polyol used to synthesize the rigid PU foam, as indicated elsewhere [99].

No differences during the foaming process (growth start time, growth rate, and final aspect of the foam) were observed between the two polyols. The only appreciable difference that was observed between the three PU foams was that the azidified foam was slightly darker than the commercial one due to the higher coloration of the azidified biopolyol [91].

The internal morphology of all the rigid PU foams was observed using a scanning electron microscope (SEM) (**Figure 9**). In all three foams, a polyhedral cell structure can be observed. A slight increase in the cell size of Foams B and C with respect to that of Foam A can be observed.

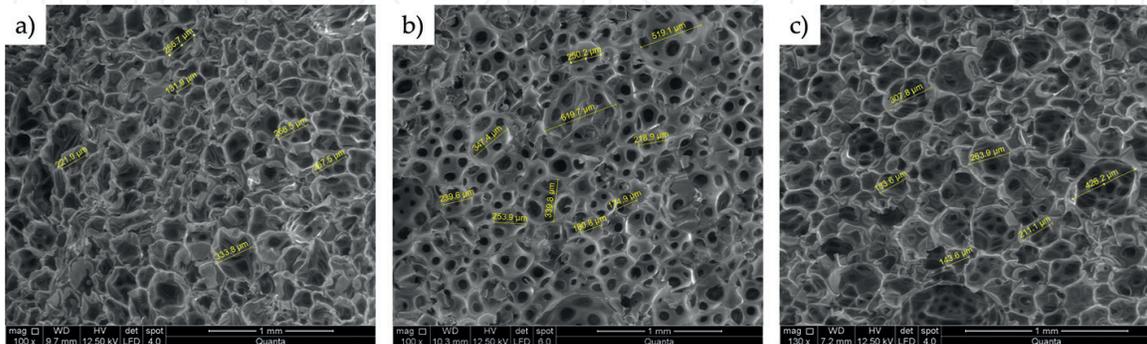


Figure 9. SEM images of (a) Foam A (synthesized from commercial polyol) (b) Foam B (synthesized from the biopolyol obtained using glycol as ring-opening agent) and (c) Foam C (synthesized from the azidified biopolyol).

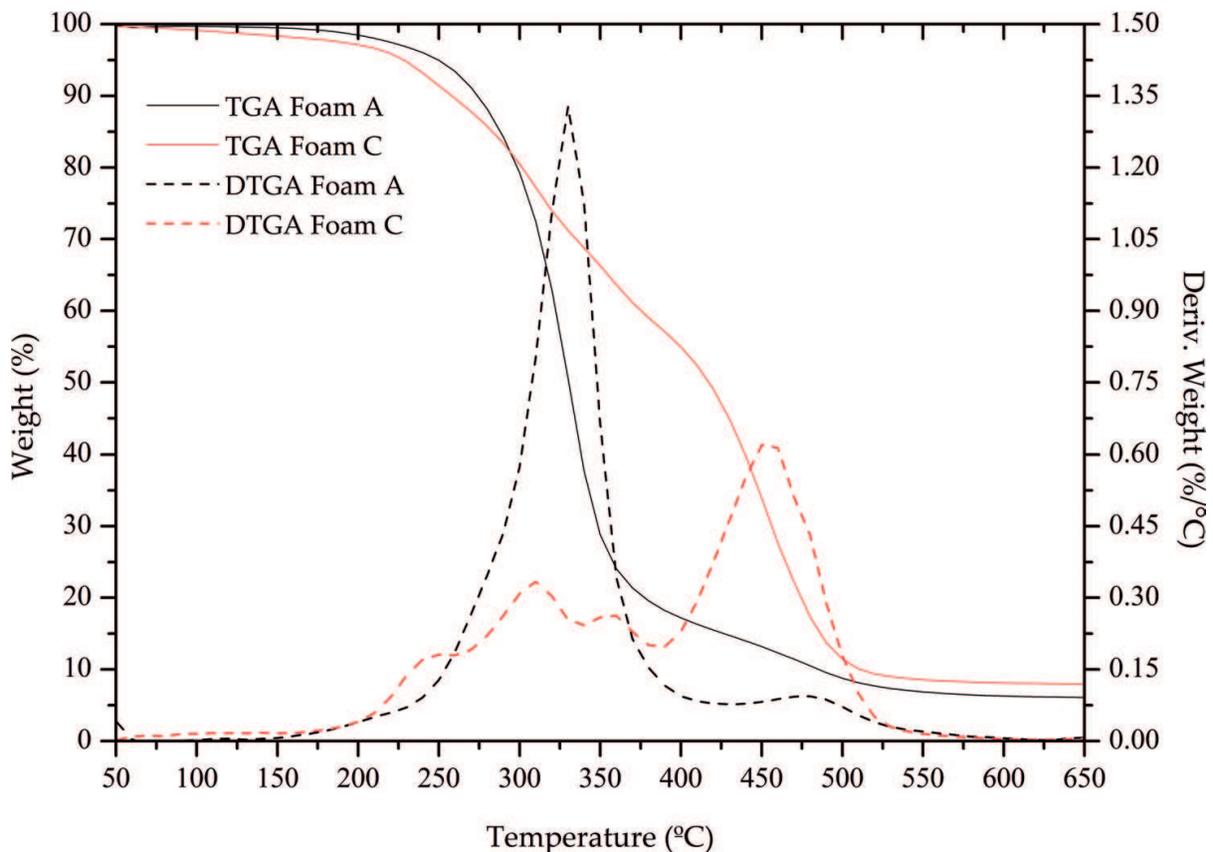


Figure 10. Comparison between thermogravimetric curves of Foam A (commercial foam) and Foam C (azidified foam).

This increase can primarily be attributed to two effects: the different volumes of pendant groups and the unadjusted foam formulation, which modify the nucleation and foaming rate.

Finally, thermogravimetric analyses (TGA) were used to investigate the effect of the incorporation of azide groups on the thermal stability of the biopolyols. **Figure 10** compares the TGA and DTG curves for Foam A and Foam C under an air atmosphere.

Two degradation steps can be observed for both polyurethane foams. The first one is assigned to the thermal degradation of the crosslinked polymer, which can be divided into hard and soft segments. The second step is attributed to the decomposition of the hydrocarbon chains formed by the main components of the foam (polyol and isocyanate) [100, 101]. As can be observed in the thermogravimetric curve, the incorporation of 0.09 g of nitrogen per gram of Foam C increased the maximum degradation temperature from 330 to 450°C. Moreover, the residue yield observed at 650°C improved from 6.28 to 8.11, indicating that Foam C is more thermally stable than Foam A. These results confirm the enhancement in the thermal stability of the PU foams because of incorporating nitrogen groups into their chemical structures by using azidified biopolyols from grape seed oil as raw materials.

5. Other non-food applications

Cosmetics are substances or products used to enhance or modify the aspect or smell of the body. During the last years, a wide sector of cosmetic consumers is expressing their interest in natural products due to the appearance of allergies and skin irritations due to the synthetic preservatives (mainly parabens), colorants, stabilizers, etc. [102]. Grape seed oil has been presented by Fiume et al. [103], as a safe alternative to these synthetic compounds, which are to be incorporated in cosmetics. Mbah [104] compared different vegetable oils with grape seed to act as lipophilic substance, indicating that it can be a potential dermal permeation enhancer. Attending to micro- and nano-structured cosmetic systems, Contri et al. [105] determined the viability of preparing grape seed oil nano-capsules for cutaneous applications, which enhanced the antioxidant activity. Moreover, Glampedaki and Dutschk [102] studied the preparation of oil-in-water emulsions using wine and grape seed oil, observing a good stability, when using glycerol monostearate as emulsifying agent.

Grape seed oil was compared with soybean and rapeseed oil for producing renewable cross-linked polyester resins by Clark et al. [106]. They concluded that grape seed oil presented a lower crosslink density due to its higher linoleic acid content but a higher thermal stability, being this product a viable substitute of traditional polyester resins in low stress or high-demanding thermal applications.

6. Conclusions

Grape seed oil is one of the main by-products of the winery industry. The fatty acid profile of this oil showed that it is mainly composed by linoleic and oleic acid, but the total amount

and proportion of this depend on the grape variety, the weather, and the extraction method. However, grape seed oil has a limited application from a nutritional point of view, since most nutraceutical compounds (vitamin E active compounds, phytosterols, etc.) remain on other by-products, mainly on the grape skin and grape seed flour. Hence, different non-food applications have been proposed and discussed along with this book chapter.

The transesterification of grape seed oil leads to the production of a biodiesel with excellent low-temperature properties. On the other hand, other quality requirements, such as cetane number and oxidation stability, cannot be easily accomplished using grape seed oil as raw material due to its high content of polyunsaturated fatty acids. However, this can be easily solved by blending the grape seed oil based biodiesel with other fuels.

The epoxidation of grape seed oil using peracetic acid formed *in situ* from acetic acid and hydrogen peroxide is a feasible process for obtaining a highly epoxidated vegetable oil. The negative effect of the secondary reactions of this process, namely the hydrolysis and further oligomerization, can be diminished by working at high temperature (90°C) and short reaction times (1 h).

Epoxidized vegetable oils, such as grape seed oil, are of high interest for producing biobased materials that nowadays are produced from petroleum. So, biopolyols can be produced from epoxidized grape seed oil using different ring-opening agents such as glycerol and sodium azide. Different rigid polyurethane foams were synthesized from these biopolyols, using a commercial petroleum-based polyol as reference material to compare the internal structure and their properties. No internal differences were observed between the foams. However, it was observed an increase on the thermal stability of the foam which incorporated N₃ groups.

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