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Antioxidative and Anticorrosive Properties of Bioglycerol

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1. Introduction

Raw glycerol fraction (also called bioglycerol) is the second product of fatty acids triglycerides alcoholysis. However, by many biodiesel producers it is treated as a waste, unwanted material. Due to overproduction of the glycerol fraction there have been many attempts to find its proper utilization, especially that it can comprise up to 30% of the whole biodiesel production. Finding proper applications for bioglycerol became a research target of scientists from all over the world (project E! 3590 Use-Glycerol: New concept for utilization of glycerol fraction from biodiesel production, http://www.eurekanetwork.org/project/-/id/3590, Corma et al., 2007, Pagliaro et al., 2007). What is important, bioglycerol has an enormous chemical potential and should be considered as a valuable transesterification product and thus a versatile feedstock for the creation of new chemicals (Pagliaro & Rossi, 2010). Until recently bioglycerol purification was based on the separation of fatty acids from the mixture and recycling them to biodiesel production process. There were also a few tests made to use raw glycerol fraction omitting distillation procedures. One of them was to utilize bioglycerol as an additive during composting process, especially when potassium hydroxide as a catalyst in transesterification was used. This utilization was abandoned due to the technological problems and relatively too expensive comparing with the cost of compost. On the other hand, production of pharmaceutically pure glycerol is very time and energy consuming due to its high boiling point. There is also a propano-1, 2, 3-triol overproduction, thus its price is low. Market is already flooded with glycerol-containing products especially in food, pharmaceutical, cosmetic and leather industry. That is why there arises an issue of finding new ways of biodiesel utilization. It is essential to make this fraction as valuable as biodiesel. The principal directions of solving "bioglycerol overproduction problem" are oriented towards the development of production methods for the new platform chemicals (Behr et al., 2008, Corma et al. 2007, Gu et al., 2008, Zheng et al., 2008, Zhou et al. 2008). Therefore the final products should be obtained directly from raw bioglycerol. In such case the purification process would be shifted to the final product that would have much lower boiling point or different solubility and it would be cheaper. A few trials were made to elaborate production of glycerol formals, very valuable fuel additives (Trybula et al., 2010). There was also hydrogen produced on the basis of bioglycerol fermentation (Ito et al. 2005) or with the use of catalyst (Hirai et al., 2005, Huber et al. 2003). Until now the main attempts of the studies were focused on the most abundant constituent

of the fraction – glycerol. The second direction of bioglycerol research concerns the fraction as an integrate material and takes advantage of its minor constituents. Fatty acids and alcohol are utilized by turning them back to the transesterification process. The residues of fatty acids and unreacted triglycerides can be turned into soaps or lubricants, thus the final product would contain glycerol as "an additive" (patents: Jerzykiewicz et al., 2006, PL 378802, PL 207449, Jerzykiewicz et al., 2008, PL 381066, PL 386312, Lukosek et al. 2007, PL 384164, PL 383841). Recently there were also investigations on trace components such as antioxidants performed.

The concept of the studies presented in this chapter was to find the antioxidants routes during the biodiesel production and to establish their structure. Are the antioxidants originated in oils transferred during transesterification process to the biodiesel or to bioglycerol? The antioxidants occurring in the transesterification products should have phenolic-like structure due to their vegetable oil origin. Virgin oils are rich in substances that exert antioxidant properties such as: tocopherols, phospholipids, carotenes and sterols (Velasco et al, 2005, Blekas et al., 1995, Koski et al. 2002). Chemical properties of the tocopherols lead to their better solubility in bioglycerol than biodiesel. If the glycerol fraction was the receiver of the antioxidants, these valuable compounds would be condensed there (up to 30% of the initial volume). Additionally, structural investigations would be necessary to confirm whether the conditions of performed transesterification influence the tocopherol activity. Thus apart from standard methods used for establishing the main bioglycerol constituents (gas chromatography, assays based on titration) more advanced methods are indispensable. One of the most reliable techniques for detection as well as quantitative characterization of the antioxidants is electron paramagnetic resonance (EPR) spectroscopy. Apart from direct EPR measurements of free radicals and other paramagnetic species the method allows studying diamagnetic compounds like phenolic antioxidants by the use of spin trapping or radical scavenging techniques.

2. Bioglycerol – What it is?

Bioglycerol is a mixture of: propano-1, 2, 3-triol, residues of alcohol, soaps, fatty acids esters, mono-, di-, triglycerides, phospholipids and some minor constituents. The most popular method helpful in determination of the fraction composition is gas chromatography. Presented in the chapter results of glycerol fraction composition were analyzed using gas chromatography (GC) (Hewlett-Packard, model 5890 GLC II). The chromatograph was equipped with a flame ionization detector (FID) and 11 m x 0.22 mm x 0.1 μm high temperature capillary Utra-2. Separation of esters C-18:1, 2, 3 was achieved by the usage of HP-FFAP capillary column. Argon was used as a carrier gas at a flow rate of 2 ml/min. The column temperature was increased from 100°C to 380°C, at the rate of 15°C/min. This last temperature was maintained for 2 minutes.

Data obtained from chromatography concern only glycerol, traces of different esters and between fractions. It has to be kept in mind that to establish more details about chemical properties of the fraction there are also titration methods necessary in order to determine saponification number and a soap content. As a standard procedure bioglycerol is preliminarily distilled to remove water and alcohol. Then the percentage data obtained from gas chromatography are recalculated according to the soap, water and alcohol contents.

An exemplary data of several bioglycerols (table 1), chosen as representative from about forty investigated samples, were derived from producers using different catalyst (NaOH for

W and K; KOH for the rest of the samples), different alcohol (ethanol for W, methanol for the other samples) and different oil (W- waste, used frying oil; Z, K – rapeseed oil, T – mixture of pure, waste oils and animal fats). The results show that the proportion of constituents can be very versatile. It depends mainly on the technology used by producers and is strongly influenced by the type and diversity of lipids used. Some producers apply pure rapeseed oil as an input material, some pure palm oil or a mixture of used, waste oils and animal fats. What is more, different alcohol (methanol or ethanol) and catalyst can be used. Finally the resulted bioglycerol mixtures might vary in fatty acid (more or less unsaturated), antioxidants and other natural compounds originated in oils, content.

Component [%]		**Z**			**T**	
	W	**Z1**	**Z2**	**K**	**T1**	**T2**
Glycerol	79	60	96	57	60	70
BF	0.35	0.21	0.69			
FAME C-16:0		0.21	0.2	0.42	0.24	0.11
Acid C-16	0.6			0.28	0.72	
FAME C-18:(1-3)	0.36	4.17	0.63	7.6	4.2	
BF		0.24	0.15			
Acid C-18	0.13			0.2	6.0	1.3
Acid C-18: (1:3)	2.45	1.41				
BF	0.54	0.71				
FAME C-20:0				0.2		
Monoglycerides		3.09		1.8	2.2	1.9
Diglycerides		0.04				
Triglycerides	0	0	0	0	0	0
Soaps	20.9	19.7	2.15	32.4	26.6	26.1
Water & alcohol	28	17.7	22.3	23	16.7	6.8
SN [mgKOH/g]	0.67	25.7	0	31.5	34.5	9

Table 1. Composition of exemplary glycerol fractions (BF- between fraction, SN - saponification number, FAME - fatty acid methyl/ethyl ester).

As it is shown in table 1 even composition of bioglycerols from the same producer (Z1 and Z2; T1 and T2) can be very different. In this case content of the fraction depends more on the specific conditions during the time of the production, than on the materials used. It suggests that the main significance is due to an accuracy of the technology processing.
Alcohol removed from bioglycerol is returned to the transesterification process. Some producers additionally perform purification processes such as acidification and separation of lipid residues such as fatty acids, which can be then recycled to the process. Application of this step leads to the formation of additional two fractions – fatty acids with low glycerol content (3-6%) and acidified, more condensed glycerol fraction.

3. Antioxidants content studies

The analytical methods based on the standard procedures determine only the main bioglycerol constituents content. In order to establish antioxidant presence and oxidation stability additional methods need to be employed. Popular techniques dealing with the problem are

UV-Vis or Electron Paramagnetic Resonance (EPR) spectroscopies (Papadimitrou et al., 2006, Jerzykiewicz et al., 2009, Jerzykiewicz et al., 2010, Jerzykiewicz et al. 2011).

3.1 Folin-Ciocalteu assay

The most common method for the quantitative studies of antioxidants in natural substances is the Folin-Ciocalteu (FC) assay (Roura et. al. 2006, George et al., 2005) concerning UV-Vis measurements of investigated substance with the Folin-Ciocalteu reagent (FCR). It is also called the Gallic Acid Equivalence method (GAE) due to the gallic acid application as the reference compound (Singleton and Rossi, 1965). However, caffeic acid (Koski et al. 2002) is also commonly used in such investigations. The FC analysis is based on the reaction of the reagent (a mixture of phosphomolybdate and phosphotungstate) with reductive (antioxidant) compounds. Measured at 765 nm signal intensity gives information about amount of the substance required to inhibit the oxidation of the FCR. Although it is used as the standard method in the investigation of phenolic antioxidants in natural mixtures of plant origin like oils and fruits, it is not a reliable one in the bioglycerol studies. The main disadvantage (known from 40ties of bygone century) of the method is that not only the phenolic antioxidants react with the FCR (Abul-Fadl, 1949, Ikawa et al., 2003, Everette et al., 2010). The reaction can be influenced (inhibited or accelerated) by several factors (George et al., 2005). In case of bioglycerols the reaction is mostly induced by metal ions (like potassium ions from catalyst), but there also exists a range of different factors (organic and inorganic compounds) which may falsify the results and hence make them incomparable among the bioglycerol samples. Additional problem concerns partial insolubility of the bioglycerol in water solution which extorts change in the Folin-Ciocalteu procedures. Generally for such samples an extraction (Koski et al. 2002) is performed, then extract is tested. However, there might be new problem generated, with the efficiency of the extraction. Another issue is the fact that not every type of antioxidant may be transferred to the solvent used in extraction and some losses of the investigated substances are possible. Too many factors influence the FC method and thus make it inadequate to be recommended for glycerol fractions analysis.

3.2 EPR spectroscopy

The method which allows investigations of the natural mixtures without their previous purification and separation is the Electron Paramagnetic Resonance (EPR) spectroscopy, called also Electron Spin Resonance (ESR). EPR is based on the interaction of unpaired electron of the compound with the magnetic field, which induces splitting of the energy of unpaired electron spin (Zeeman splitting effect). Created two (or more) energy levels enable absorption of microwave frequency radiation. The EPR signal is usually recorded as a first derivative (dA/dB), of the absorption (A). Shape of the absorption signal can be approximated by a Gaussian or a Lorentzian curve, or as the mixture of both. When measurements are performed there are only compounds with unpaired electron detectable (unlike the rest of the constituents). This property is essential in the studies of minute quantities of paramagnetic species and due to this very complex mixtures can be investigated without previous purification. The intensities and width of lines detected using EPR spectroscopy enable quantitative calculations of the paramagnetic species (N_x on figure 1). Application of quantitative standards gives the absolute values of spins per gram. The fundamental EPR parameter, g, exhibits the structural properties of the electron. For free electron the parameter is equal 2.0023 and variations from this value provide important

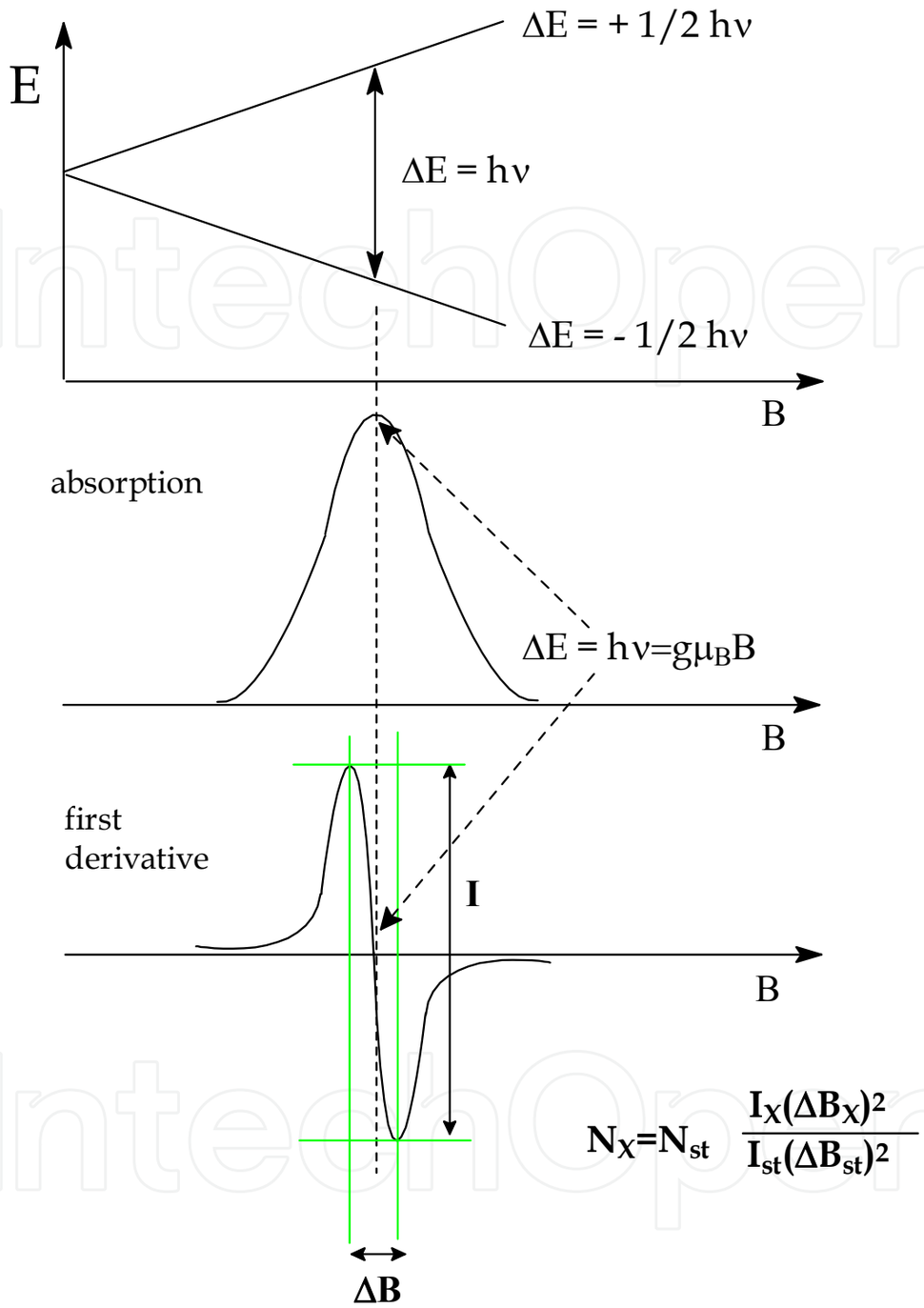


Fig. 1. Zeeman splitting of energy levels of an electron placed in magnetic field (A – absorption, B- the magnetic field, μ_B-Bohr magneton, ν – frequency, h- Planck constant). For quantitative calculations: I_X, ΔB_x– intensity and width of investigated line, I_{st}, ΔB_x–, N_{st}– intensity, width and spin concentration of standard line).

information about the structure of an electron neighborhood. For π-type of organic radicals g-parameter is generally higher than for σ-radicals (Gerson and Huber, 2003, Lund et al., 2011).

The g parameter can be calculated directly from the spectrum. Radical structure can be also described on EPR spectra by the hyperfine splitting occurring when spin of unpaired electron interacts with non-zero spin of nuclei. The number and intensity of the lines split depend on the value of the nucleus spin (1/2, 1, 2/3…) and number of the interacting nuclei.
The EPR spectroscopy has already been used as a helpful tool in the studies of oxidative properties of edible oils and other food products (Papadimitrou et al. 2006, Jung & Min, 1992, Vicente et al. 1995, Andersen & Skibsted, 2001). Investigations concerning oxidative properties of bioglycerols are not very common and widely applied. Authors performed such research for all the transesterification products and an input material. Presented herein results were executed on Bruker spectrometers from Elexsys series.
At the beginning of the oxidative stability research of investigated mixtures (different oils and its products: biodiesel and bioglycerol) were subjected to the direct EPR measurements. Especially interesting results were obtained for bioglycerols. EPR spectra revealed the existence of the free radicals of semiquinone-like structure (figure 2) in these fractions.

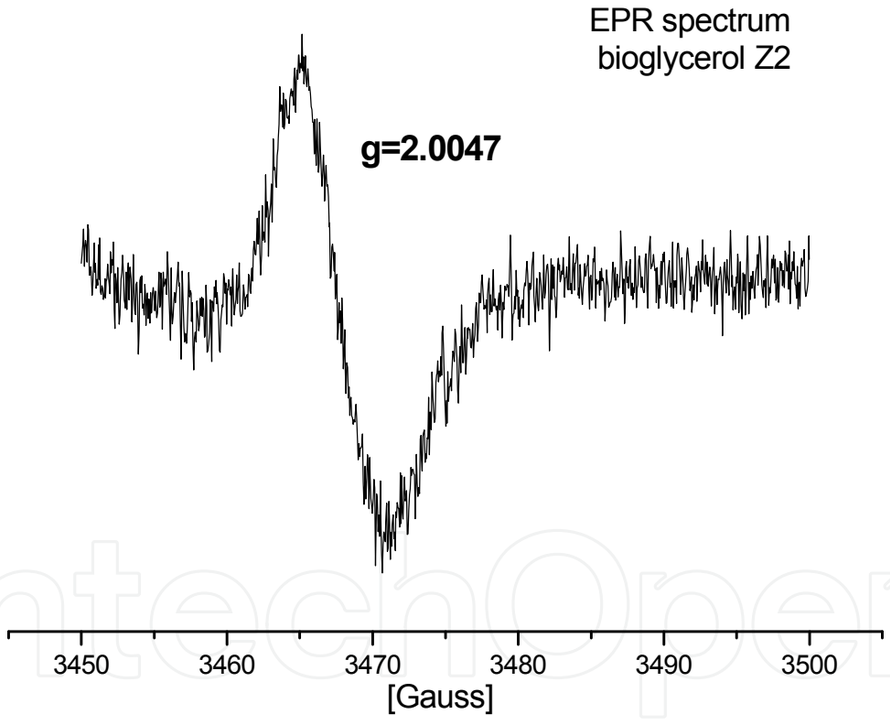


Fig. 2. EPR spectrum of glycerol fraction Z2. Five scans accumulated.

The calculated from the spectra g parameter was in a range from 2.0043 to 2.0047, which is characteristic for an unpaired electron situated on oxygen substituted to the aromatic ring (Gerson & Huber, 2003)– typical structure of poliphenolic antioxidant. This sort of the radical (semiquinone type) exists in the mixtures in quinone – semiquinone - hydroquinone equilibria. They can be easily shifted (i.e. by pH change) towards one of the forms, which in consequence changes radical concentration. They are also sensitive to metal ion binding and depending on metal type the radicals concentration can be increased (s and p shell metals)

or decreased (d shell, i.e. Cu(II), Mn(II)) (Jerzykiewicz et al. 2002, Jerzykiewicz, 2004). Formation of radicals in bioglycerols may be the result of high pH during the transesterification process caused by the application of basic catalyst. Stability of detected in bioglycerols radicals is also an important feature apart from the g parameter and concentration. They were found to be very permanent and their EPR spectra remained unchanged even for a few years!

The radicals concentration was too small to be measured quantitatively (spectra had to be accumulated 5-10 times), but they were the direct proof of phenolic systems existence in glycerol fractions, which from now on became the subject of more advanced studies. The radical of phenolic origin was not observed for every bioglycerol. Samples of technical grade purity (or higher) did not exhibit any radical signal at all.

3.2.1 EPR studies of free radical scavenging

EPR spectroscopy allows to detect only paramagnetic species on the spectrum, but the method can be also employed in the investigation of non-paramagnetic compounds. For this purpose free radical scavenging EPR method is used, where standard, stable radical (TEMPO, galvinoxyl, TEMPOL, DPPH) is employed. The radical during reaction with the investigated substance becomes a non-radical species hence as a result the decrease (scavenging) of the radical signal is observed. Progress of the reaction is calculated by the double integration of the EPR spectrum. Properly performed experiment allows to obtain the content of the investigated compound with high accuracy. In antioxidants studies the most popular radical scavenged by these bioactive compounds is galvinoxyl called also Coppinger's radical (figure 3) (Gerson & Huber, 2003, Ramadan et al. 2003).

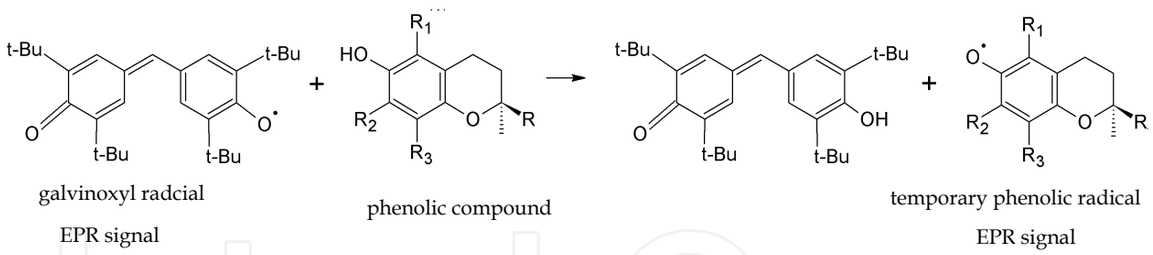


Fig. 3. Reaction of galvinoxyl radical (on the left) with phenolic (tocopherol like) compound.

The EPR signal of galvinoxyl radical (figure 4) is a well-known doublet of quintets: hyperfine splitting originates from four equivalent hydrogens situated on aromatic ring and from the hydrogen of C-H group joining the aromatic rings. The proper distinguishing of hyperfine parameters is not always possible, because the signals in the centre overlap and in some cases lines may not be separated. An attention should be paid when performing experiments in the solvent reacting with galvinoxyl (eg. toluene). Galvinoxyl radical in the described on the figure 3 reaction becomes diamagnetic and from the investigated phenolic system temporary radical is formed. This newly formed radical can also be recorded (figure 5), but mainly quenching of galvinoxyl radical is observed. As the result, in most of the situations the only change observed on the spectra is a decrease of the galvinoxyl radical signal intensity. A decrease of its intensity is the measure of reaction progress thus the antioxidant content in the investigated mixtures.

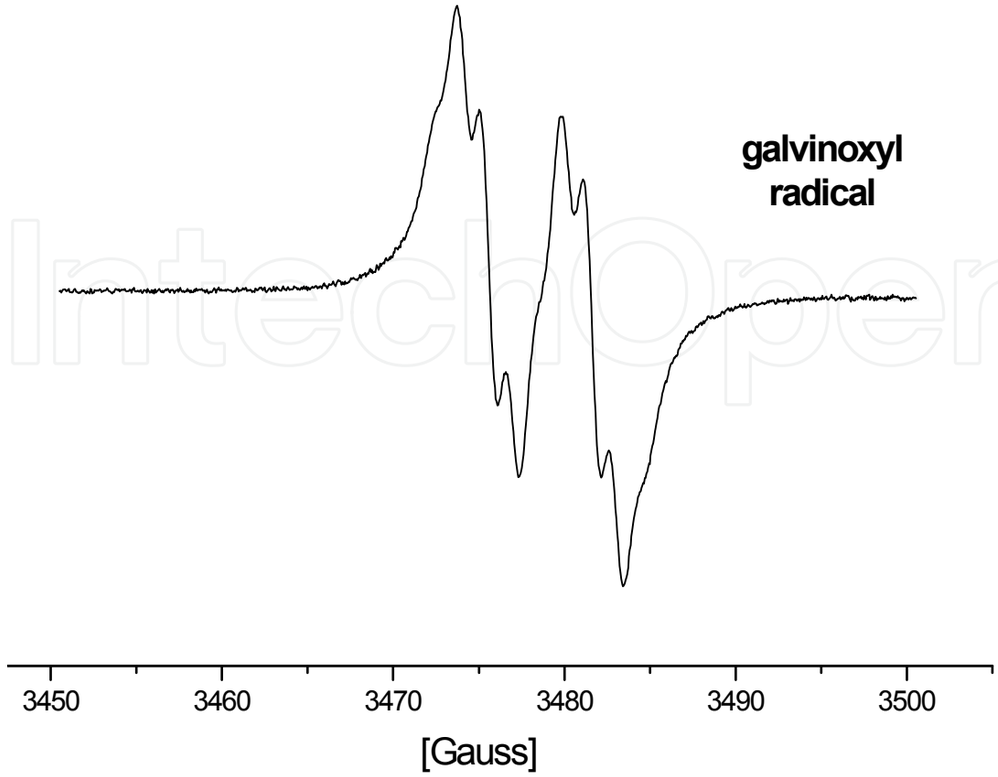


Fig. 4. EPR spectrum of galvinoxyl radical

Procedure of galvinoxyl scavenging assay using EPR spectroscopy

19 mg of sample diluted in the 200 µl of solvent
200 µl of galvinoxyl radical solution (1.1 mmol /l)
Ethyl alcohol as the solvent for bioglycerol, hexane for oil and biodiesel
The reference sample: 200 µl of solvent and 200 µl of galvinoxyl radical solution.

Prepared samples are measured in glass capillaries (0.8 mm i.d.) kept in standard quartz EPR test tubes. The EPR signals are recorded immediately and every few minutes after the beginning of the reaction, until disappearance of the signal. For establishing quantitative data EPR signal is measured after constant period of time from mixing for all the components. Measurements are performed using EPR spectrometers at the standard parameters for free radicals, modulation amplitude 1 G, at 100 kHz magnetic field modulation, X-band frequency counter at room temperature.
The intensity of galvinoxyl radical signal is calculated by the double integration of the spectra performed using common EPR programs (i.e. Bruker WinEPR Processing).

For the quantitative interpretation of the results a calibration curve is prepared. As a reference compound there can be phenolic acid applied such as caffeic or gallic acid. Results are expressed per the chosen acid equivalents (mmol/l or g/l).

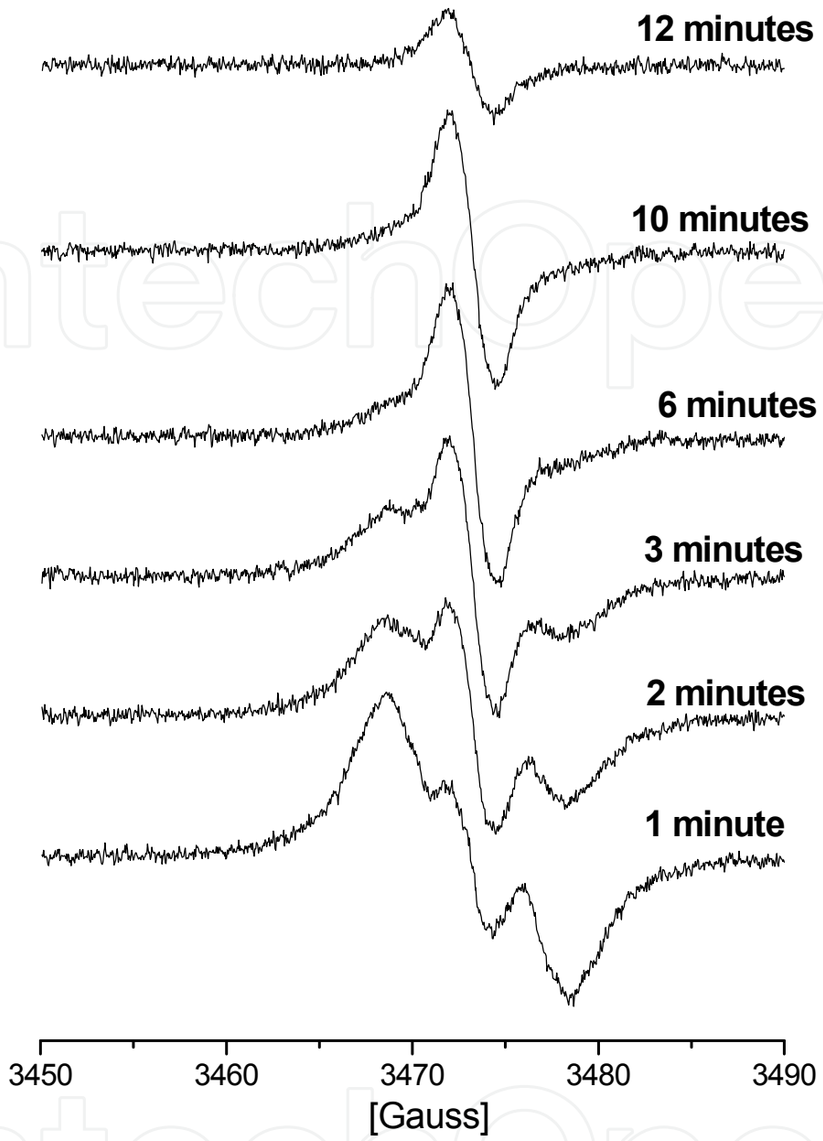


Fig. 5. EPR spectra of galvinoxyl radical reacting with glycerol fraction Z2 (ethanolic solution). Spectra were recorded at first and up to the 12th minute of the reaction.

For the presented bioglycerols the temporary radical was observed only for fractions with the highest phenolic compounds content. The g parameter of formed, unstable radical was 2.0045 – similar to the one obtained from direct studies of bioglycerol Z2, but the radicals recorded are not the same. The concentration of the transient radical is much higher, regarding dilution and recording of only one scan. What is more, scavenging measurements are performed in glass capillaries of much smaller volume than for the direct acquisition of pure bioglycerol sample in standard EPR probe (4 -5 mm diameter). The signal disappears in about 15 -20 minutes.

Intensity of the reaction depends on the concentration of antioxidant in the measured mixture. Figure 6 presents results of free radicals scavenging for four sets of samples: oils

and their transesterification products (biodiesel and glycerol fractions). As the figure clearly indicates galvinoxyl radical was scavenged by glycerol fractions much more efficiently than by oils and biodiesel samples (figure 6). That proves unequivocally that during transesterification all antioxidants occurring naturally in oils are transferred to glycerol fraction. The antioxidants in bioglycerol are condensed due to the smaller volume in comparison with the initial oil volume.

The efficiency of free radical quenching was also distinct for samples originated in various biodiesel producers. As for presented sets, each consisting of: oil, bioglycerol and biodiesel it is easy to distinguish the difference (between bioglycerol from set 1 and 2 or 3). Despite the fact that the samples are from the same producer, they do not exhibit the same quenching abilities towards galvinoxyl. More detailed studies were performed for investigated mixtures from many different producers (figure 7). Concerning the ability for the radical scavenging bioglycerols can be divided into 3 groups. In the first group there are the most efficient galvinoxyl quenchers. For this group of samples phenolic type of radical was detected during the direct measurement and a temporary radical (figure 5) found during the experiment with galvinoxyl. In this group concentration of phenolic antioxidants was also the highest. Medium content of phenols, referring to the lower antioxidant concentration was observed for bioglycerols from most of the producers and finally, there was no, or very low scavenging activity observed in the third group for analytical grade or purified in laboratory glycerol fractions.

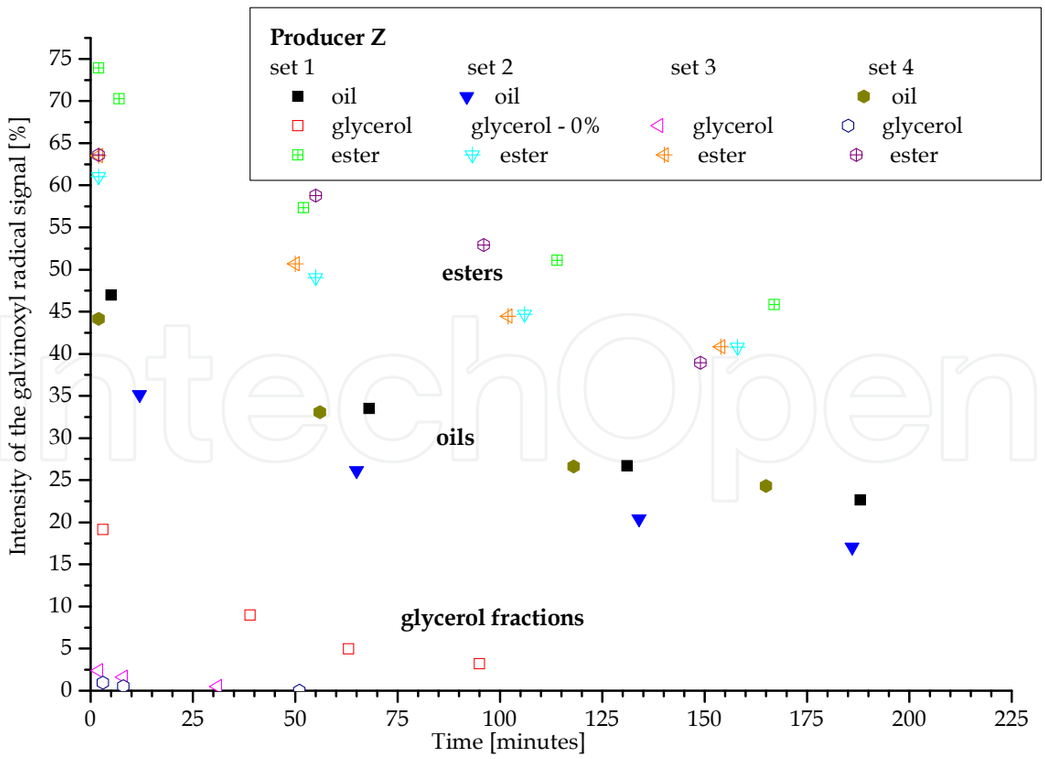


Fig. 6. Dependence of galvinoxyl radical signal intensity for oils and its products *verus* time.

Definitely it is quite easy to distinct differences which decide about scavenging properties between the first two groups and the third one. Fractions which are purified are devoided from antioxidants. Differentiation between group of high and medium scavenging properties is more complicated. Bioglycerols originated in waste oils or animal fats exhibited medium scavenging properties (second group of galvinoxyl scavengers). Explanation of this fact may be connected with the already small content of antioxidant in the input material. However, there was no correlation found between radical scavenging and soap content or saponification number estimated for bioglycerols. Glycerol fractions obtained from rapeseed oils were more diversified accordingly to the type of the process used by producer and technology rather than chemical constituency based on chromatography and other standard analyses.
Experiments with galvinoxyl not only allow to compare the radical scavenging activity between samples, but also to calculate the concentration of the antioxidants. For this purpose the calibration curve has to be prepared from the standard, model antioxidant. The most common reference compounds used are gallic and caffeic acids. There is no need to record the EPR spectra every few minutes to follow the exponential decay of galvinoxyl signal, but all the samples should be measured once at exactly the same time (in our case 5 minutes) from mixing them with galvinoxyl. Results of the quantitative EPR measurements are discussed in chapter 3.4.

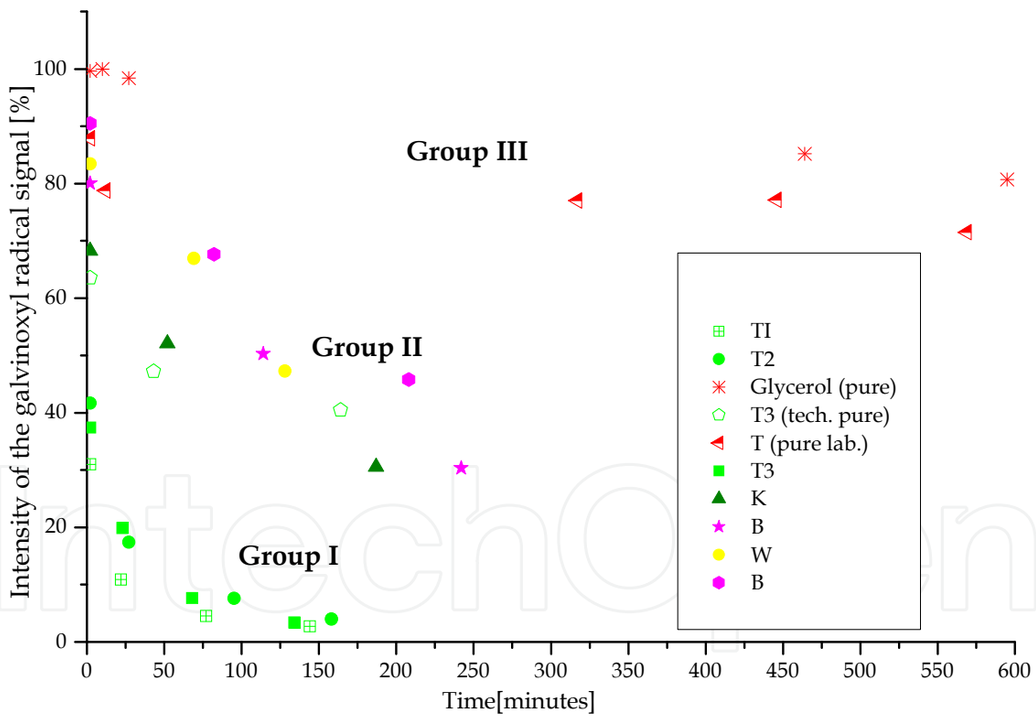


Fig. 7. Dependence of galvinoxyl radical signal intensity for the glycerol fractions from different producers *versus* time.

3.3 UV-Vis studies of free radical scavenging

Reaction of galvinoxyl with phenolic compounds can be also investigated by the use of UV-Vis spectroscopy. Preparation of the graph describing the reaction is the same as fo EPR method, but single instead of double integration of the signal is applied.

Procedure of galvinoxyl scavenging assay using UV-Vis spectroscopy
Solution A: 95 mg of bioglycerol sample dissolved in ethanol to the volume of 5 ml
Solution B: 10.6 µM solution of galvinoxyl in ethanol

Calibration curve: set of caffeic acid ethanolic solutions in concentration range from 7 to 350 µM. The standard solutions are used instead of A solution during measurements.

2 ml of solution B is placed in a cuvette and then 100 µl of solution A is added, stirred and measured after 1 minute.
An absorbance is measured at 429 nm at room temperature.

Figure 8 presents absorption of galvinoxyl signal at 429 nm (black line). Decrease of maximum absorption of galvinoxyl in time caused by the interaction of the radical with phenolic system is clearly presented after one and five minutes from the beginning of the reaction. Absorption value obtained from the spectrum is then recalculated to appropriate phenolic acid equivalent. As it is seen on the spectra (figure 8) new chemical species with absorption at 578.5 nm is created during the reaction. However, increase of the signal intensity is not linear and is not a good indicator of the reaction progress or antioxidant concentration. The main disadvantage of this method is higher volume of the solutions necessary for the measurements (1-2 ml).

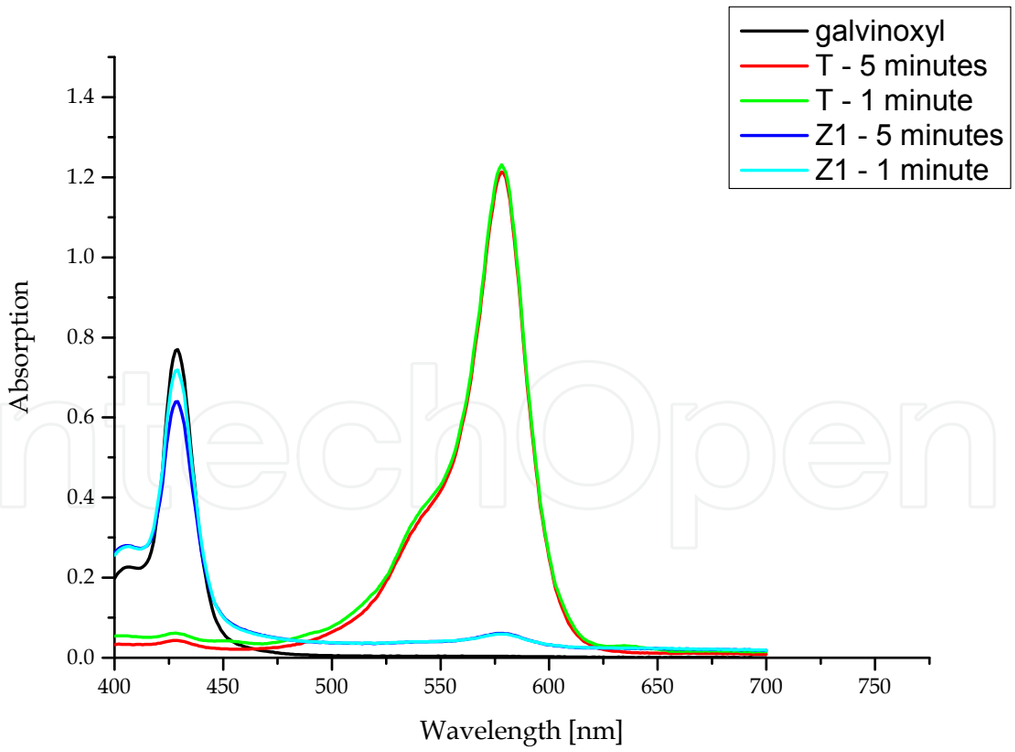


Fig. 8. UV-Vis spectra illustrating pure galvinoxyl ethanolic solution absorption (black line) and results of the reaction between radical and bioglycerol T and Z1 after 1 and 5 minutes (colored lines).

Similarly to the EPR technique also quantitative assay can be performed with caffeic or gallic acid solutions of different concentrations (calibration curves method). For this measurements there is no requirement of recording the total slope of the scavenging reaction *versus* time, but one point (as in EPR), which is obtained by measuring the absorption of galvinoxyl solution in ethanol at 429 nm. The most important is to measure the spectra at exactly the same time, for solutions of model antioxidant and for the investigated mixture (for example 1 or 5 minutes from mixing).

3.4 Comparison of different methods assaying antioxidant content

As it was mentioned above, reaction of galvinoxyl radical with phenolics was monitored using two different spectroscopies: EPR and UV-Vis. Quantitative analysis of phenolic compounds was conducted on the basis of calibration curves of phenolic acids. Results of both assays expressed in caffeic acid equivalents are given in table 2.

Bioglycerol	Phenolic antioxidant content [g/l]	
	UV-Vis	EPR
O	0.025	0.023
W	0.0060	0.0045
B	0.0091	0.012
A	0.010	0.0088

Table 2. Phenolic antioxidant content calculated for caffeic acid as the standard for bioglycerol from different producers (W- waste oil and NaOH as catalyst, rape seed oils: O – as catalyst NaOH, B – laboratory scale, A – commercial scale).

Results obtained from EPR and UV-Vis spectroscopies are comparable. However, it has to be kept in mind that both methods assign species based on their different properties. EPR detects only paramagnetic species, that is why EPR spectroscopy is more selective. Another advantage of EPR is that it uses smaller quantities of the investigated samples. However, EPR instrumentation is incomparably more expensive than in case of standard UV-Vis spectrometers. On the other hand EPR spectrometers have became more popular in industrial laboratories due to small, easy to use apparatus evaluable on the market. Till now the computer-size spectrometers are dedicated for analysis of food and beer quality and there is no obstacle to use them in oil products standard analysis.

Apart from spectroscopic methods also classical, analytical procedures were helpful in the studies of antioxidant properties of bioglycerols. One of these methods is a standard Herbert test, which also proved anticorrosive properties of bioglycerols. Before measurements all fractions were saponified (according to the Patent by Jerzykiewicz et al., PL378802) and solutions of different initial and final soap content were used for analysis. The standard Herbert tests were performed using special steel plates with the surface of 25 and 43 cm^2. The plates were initially weighted and then were kept at room temperature for the 120 h in the saponified solutions. As it was expected the corrosivity of all saponified bioglycerols decreased with the increase of the soap content, which was crucial for the results. The sample of low initial soap content, even having the same final soap content to another bioglycerol samples of different constitution, exhibited much better anticorrosive properties

in Herbert test. The same bioglycerols were found to be the best free radicals scavengers in galvinoxyl experiments.

4. The antioxidants structure

Depending on the origin of the bioglycerol antioxidants present in the mixtures can have different structure (figure 9). Composition of tocopherols, tocotrienols and carotenoids, the substances responsible for antioxidant activity in oils, vary depending on the source of an input material. Naturally occurring antioxidants in oils belong mainly to the group of tocopherols. α-Tocopherol is considered to be predominant antioxidant in olive and sunflower oils (Velasco et al, 2005, Blekas et al., 1995, Koski et al. 2002) while γ-tocopherol prevails in rapeseed oil (Velasco et al., 2005, Koski et al. 2002). The content of antioxidants depends also on the type of oil purification procedures (cold-pressed, refined). Refining removes about 40% of tocopherols and 98% of carotenoids (Koski et al., 2002).

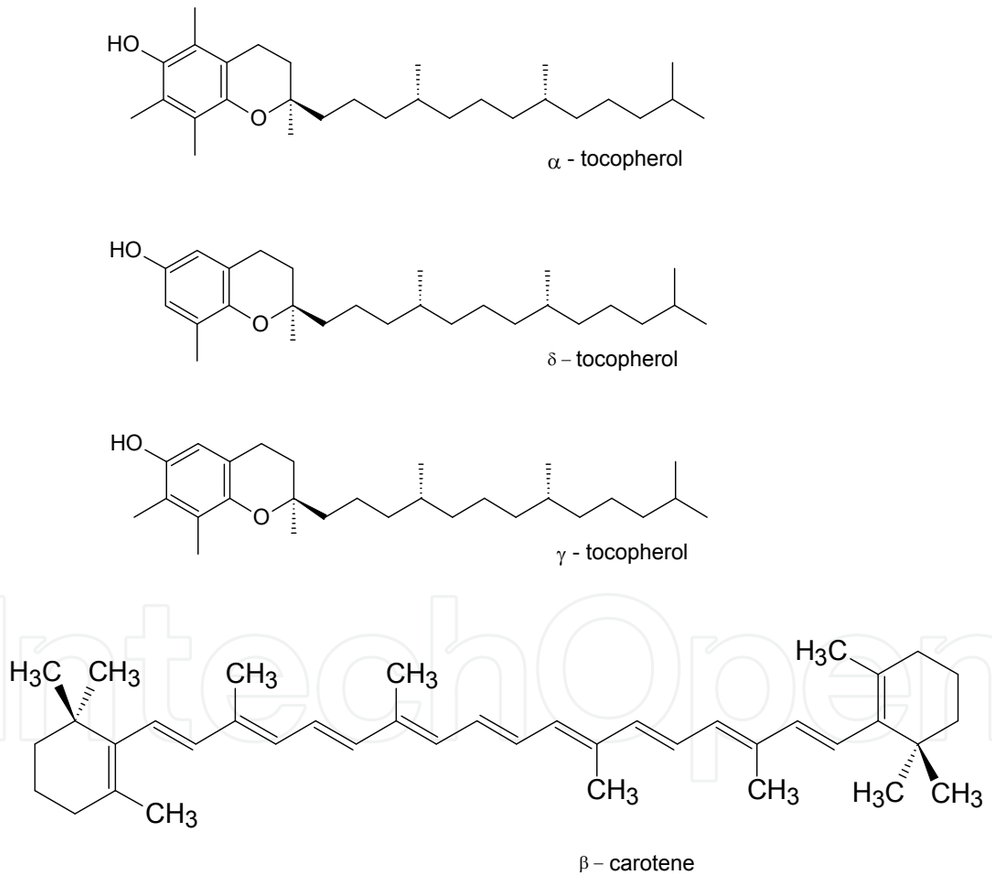


Fig. 9. Exemplary structures of antioxidants present in virgin oils.

Establishing the structure and type of antioxidants found in bioglycerols is an additional problem in the studies. What is more, the antioxidant structure might change during the transesterification process. To solve this puzzle EPR spectroscopy spin trapping technique was used accompanied by DFT calculations (Jerzykiewicz et al., 2010). The structure of active antioxidants was investigated by the studies of temporary radicals formed upon

oxidation reactions. During oxidative stress in such a complex mixture as glycerol fraction different, transient, unstable radicals can be formed. These radicals have their origin in the oils or fats constituents such as tocopherols, lipids and glycerol. All these species have different structure and can be easily distinguished by their EPR parameters. However, they are too reactive and recombine too quickly to be measured directly by EPR spectroscopy. Investigation of such unstable radicals is possible when spin trapping technique is applied.
Spin trapping technique is based on the reaction of the stable diamagnetic compound (a spin trap, non-radical species) with the short- living radical (figure 10). On the figure 11 there are the structures of different spin traps given, such as: PBN (N-t-butyl-α-phenylnitrone) and another commonly used nitrones: DMPO (5,5-Dimethyl-1-pyrroline N-oxide) (Dikalov & Mason, 2001) or POBN (α-(4-Pyridyl N-oxide)-N-tert-butylnitrone). The choice of a proper spin trap for the experiment depends mainly on its solubility and reactivity (McCormick et al. 1995). In case of research of substances originated in oils such as glycerol fractions the best spin trap applied is PBN due to its high solubility in lipids.

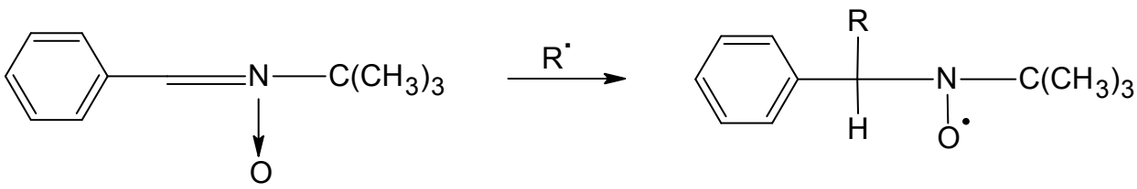


Fig. 10. The PBN (N-t-butyl-α-phenylnitrone) spin trap reaction with unstable radical (•R), as the result stable PBN/•R spin adduct is formed.

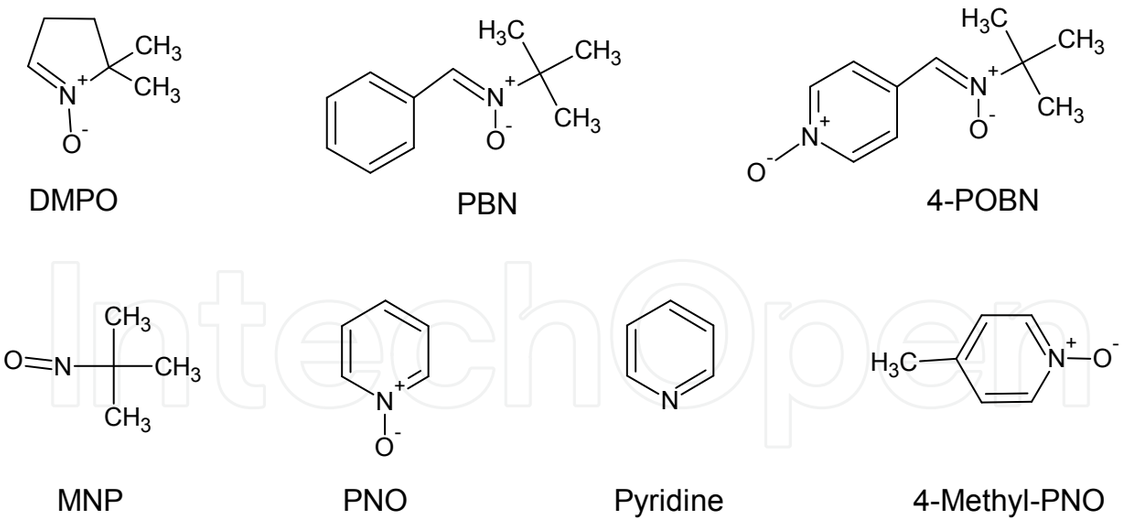


Fig. 11. Comparison of different spin traps formulas.

A spectrum of PBN adduct consists of triplets of doublets - three lines reflecting hyperfine interaction of unpaired electron with nitrogen nucleus and each of these lines split into two – interaction with hydrogen nucleus. The parameters of the splitting constants, A_N and A_H (for the nitrogen and hydrogen nuclei, respectively) depend on the type of radical trapped and are used as a source of structural information about it. Computer simulation of EPR

spectra allows to identify the nature of the radicals as oxygen-, nitrogen- or carbon-centered. The parameters are also helpful in differentiation between the size of the group attached to the spin trap (big or small adducts) (Janzen and Blackburn, 1968, Jerzykiewicz et al., 2011, Jerzykiewicz et al., 2010). What is more, spectra of adducts allow to perform quantitative studies of formed radicals.

In the described experiment apart from bioglycerol samples a few reference compounds such as: α- and δ- tocopherols, oils, different triglycerides, fatty acids and pure glycerol were used in analogous experiments.

The EPR spectra of bioglycerols exhibited typical splitting pattern for the PBN adducts (figure 12), but the hyperfine parameters changed in time of the experiment and were dependent on the glycerol fraction composition and antioxidant content. In the beginning of the oxidation all bioglycerols exhibited spectra with the same hyperfine parameters as recorded for the adduct of PBN with radical from α-tocopherol (table 3, figure 12). They were distinctively different from parameters obtained for PBN/•δ – tocopherol adduct. This fact indicates that antioxidants in bioglycerols have a structure of α – tocopherol. During the experiment, values of hyperfine coupling constants underwent change in comparison with the initial ones. Week or two from the beginning of the experiment, the spectra recorded for bioglycerols, where previously described free radicals scavenging investigation proved the lowest antioxidant content, exhibited spectra of different shape (broadening of the signal) and parameters values. On the contrary spectra of bioglycerols with the highest antioxidant content remained unchanged until the total disappearance of the signal (even 3 months). The change of hypefine parameters, found for the samples of smaller antioxidant content, especially reduction of A_H parameter (~2.0 G) indicate trapping of a radical group of a bigger size. Comparison of the spectra and parameters calculated from them with the values obtained for reference

Procedure of spin trapping assay

Solution A: PBN 0.067 M solution (in ethanol, acetone, DMSO or ethyl acetate)
Soultion B: 3 % H_2O_2 (in respective to PBN solution solvent)

250 mg of bioglycerol dissolved in 0.5 ml of solution A. To the homogenous solution 0.125 ml of solution B is added and stirred.

Prepared samples are measured in glass capillaries (0.8 mm i.d.) kept in standard quartz EPR test tubes. The EPR signals are recorded 10 minutes and 1 hour after mixing. Later mixture is sampled and measured every day and afterwards every few days till the complete disappearance of the signal. In order to establish the hyperfine parameters of the spectra simulation should be performed using appropriate programs (i.e. Bruker WinEPR Simfonia).

Solvents different than ethanol may be used, however it has to be kept in mind that DMSO and ethyl acetate form methyl and methoxyl radicals in described conditions. As a result adducts of these radicals could be formed with PBN instead of radicals from α-tocopherol or lipids.

Measurements are performed using EPR spectrometer at the standard parameters for free radicals at 100 kHz magnetic field modulation, X-band frequency counter at room temperature at five replications due to the low intensity of the signals.

compounds solutions showed that similar hyperfine parameters were observed for oxidized oil samples and triglycerides or fatty acids. Despite the high content of glycerol in every glycerol fraction, PBN adduct with glycerol was not observed on any of the spectra. Parameters for PBN adduct with pure glycerol are given in table 3.
Oxidation of bioglycerols was then dependent on the constituency of the fraction. Samples, where α – tocopherol content was the highest were protected by its antioxidant properties, whereas for the bioglycerols with medium and low α – tocopherol concentration oxidation was inhibited until the exhaustion of the antioxidant. When α – tocopherol was consumed oil residues of the fractions were oxidized and typical PBN/•lipid adducts were found on the EPR spectra. Similar experiments performed in DMSO as a solvent exhibited different type of adducts. Instead of adducts originated in antioxidants or lipids, adducts derived from the solvent were observed. Methyl radicals generated in DMSO and oxidized to the methoxyl ones were then trapped by PBN. It is essential to underline, that samples with high α – tocopherol content inhibited oxidation of methyl radicals, thus PBN adducts with methoxyl radicals were not observed on the EPR spectra.

	Antioxidant concentration	First day		1 week		3 weeks	
		$a_{iso}(^{14}N)$	$a_{iso}(^{1}H)$	$a_{iso}(^{14}N)$	$a_{iso}(^{1}H)$	$a_{iso}(^{14}N)$	$a_{iso}(^{1}H)$
T1	5.75	15.3	3.8	15.3	3.8	15.3	3.8
Z1	5.88	15.3	3.8	15.3	3.8	15.4	3.7
Z2	2.17	15.3	3.8	15.3	3.5	15.3	2.4
T2	0.20	15.3	3.8	15.3	3.2	15.5	1.8
L2	0.044	15.5	3.2	15.4	2.1	15.3	1.9
α-tocopherol	n/a	-	-	15.3	3.9	15.3	3.8
δ-tocopherol	n/a	-	-	15.5	3.3	15.4	2.2
O2	n/a	-	-	14.5	2.0	15.1	1.9
1,2,3-propanotriol	n/a	-	-	14.6	2.6	14.6	2.7

Table 3. Antioxidant concentration (mmol/l) calculated per caffeic acid equivalents and isotropic hyperfine coupling constants (in Gauss) of PBN adducts (ethanolic solutions) in different period of time after reaction started. (from Jerzykiewcz et al. 2010)

Additionally, for better understanding of the reactions occurring upon oxidative stress several standard mixtures, mimicking the bioglycerol systems were prepared in different solvents. The mixtures contained of pure glycerol, triglyceride (glyceryl trioleate or glyceryl trilinolenate), α – tocopherol; pure glycerol, fatty acid (linolenic acid or oleic acid), α-tocopherol, pure glycerol and α - tocopherol. Similar mixtures were prepared also without addition of α – tocopherol. The best bioglycerol mimicking properties were found for the samples consisted of: glycerol, triglyceride and α – tocopherol. When triglycerides were exchanged for fatty acids the oxidation processes observed for the mixture via PBN adducts exhibited much different pattern than for bioglycerols. Similarly samples of glycerol and α – tocopherol only, exhibited different EPR spectra than bioglycerol.

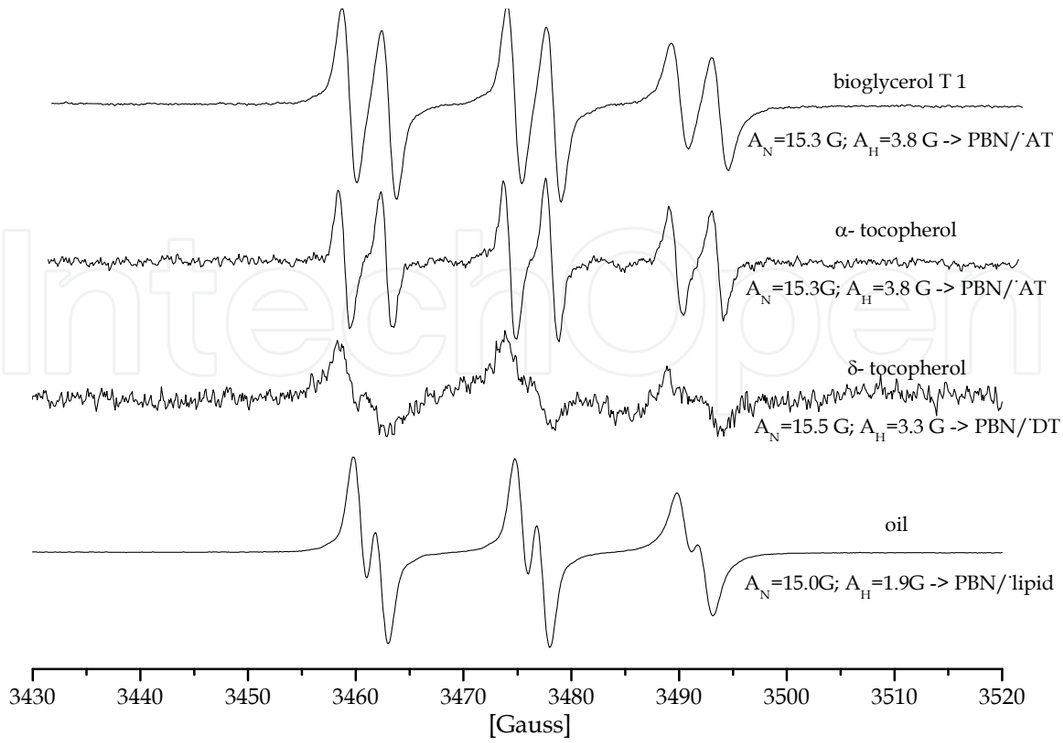


Fig. 12. EPR spectra of the PBN spin adducts formed upon oxidation of bioglycerol, α-, δ-tocopherol and oil.

Surprisingly, the DFT calculations of several possible PBN adducts with radicals of α – tocopherol origin indicated carbon-, not oxygen- centered type of the radicals trapped. This fact suggests a more complex processes associated with antioxidant activity perhaps through non-phenolic groups. This effect was stimulated in our case by the use of the radicals from H_2O_2 against α – tocopherol. Therefore, α-tocopherol exposed to reactive oxygen species, even after exhaustion of its phenolic antioxidant capability, underwent formation and trapping of different types of carbon – centered radicals. Of course it has to be kept in mind, that oxidation initiated by different reactions (i.e. photolysis) or in different solvents may result in creation of another kind of radicals (Rosenau et al., 2007).

When discussing the EPR parameters of the trapped radicals it is very important to take special consideration on the solvent used for measurements. Especially, when like in ethanol solution hydrogen bonds could interfere with the investigated radical. Thus, in the DFT calculations "solvent effect" was incorporated using Tomasi's polarized continuum method (PCM) and additionally the explicit solvent molecules were included.

The solvent effect was easily found on the spectra, according to the previous Works of Janzen group (Janzen et al., 1982) on different types of radicals trapped by PBN. Hyperfine parameters such as A_N and A_H depend on the polarization of the solvent ($E_T(30)$). The difference between parameters obtained for different solvents is small but noticeable. The bigger the polarization, the higher the EPR hyperfine parameters are. Respective values to A_N = 15.4 G and A_H = 3.8 G for ethyl alcohol ($E_T(30)$=51.9) are smaller for acetone A_N = 15.1 G and A_H = 3.5 G ($E_T(30)$=42.2). This is very important fact when considering experiments of the trapped radicals in different solvents.

5. Conclusions

Raw glycerol fraction (bioglycerol) is a product of transesterification process. This mixture (although treated by producers as unwanted waste) is a valuable source of chemicals. Apart from well-known main constituents like: glycerol, fatty acids, triglycerides or residues of alcohol it also consists of some minor compounds. With the use of EPR spectroscopy we proved that some of these minor components originated in oils are transferred during the biodiesel production process to bioglycerol. Reactions of these phenolic compounds consisted in glycerol fraction with galvinoxyl radical showed free radical scavenging properties of bioglycerol. This method developed with the usage of EPR or UV-Vis spectroscopy was much more helpful in the investigations of antioxidants concentration than popular Folin-Ciocalteu assay. Concentration of the antioxidants was different for bioglycerol samples obtained from various biodiesel producers and is strongly affected by the technology and an input material applied.

Structural investigations based on EPR spin trapping technique proved the existence of α – tocopherol type of antioxidants in bioglycerols. Upon oxidative stress unstable radicals react with PBN spin trap and create stable radicals adducts. The parameters of the adducts compared with several standard substances proved that the carbon - centered α- tocopherol radical was trapped. The structure of the radical was also confirmed by computational analysis (DFT method). Although the concentrations of α-tocopherol type phenolic compounds in bioglycerol is higher comparing with oils (where they originate from) it still exhibits antioxidant properties. It is important, according to a well-known fact (Blekas et al., 1995, Jung & Min, 1992) that too high concentration of antioxidants causes opposite effect, thus α-tocopherol can therefore behave as prooxidant accelerating oxidation reactions. For all the investigated samples this effect was not observed.

Results presented in the chapter show usefulness of EPR spectroscopy in the studies of antioxidant properties of bioglycerols both qualitatively and quantitatively and were confirmed by the other spectroscopic and non-spectroscopic methods.

The high content of antioxidants in bioglycerol (comparing with its source – oil) and the positive anticorrosive Herbert tests indicate new possibilities of usage for the fraction without very time and energy consuming purification procedures. Although bioglycerol is still a complex mixture of different components it is the potential substrate for the production of anticorrosive surfactants for technical demands. Products like shampoos obtained on the basis of the bioglycerol for car or track washing purposes will consist of glycerol, soaps and antioxidants. Additional usage offered is connected with lubricant industry. The anticorrosive lubricant may be a very valuable product, especially in machine tool and automotive industry.

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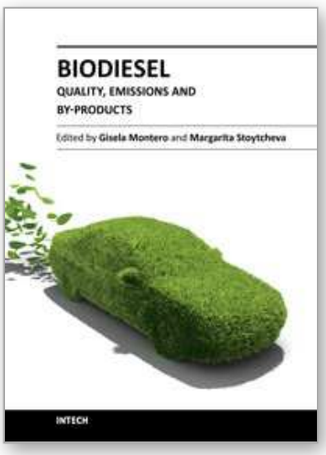
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Biodiesel- Quality, Emissions and By-Products

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This book entitled "Biodiesel: Quality, Emissions and By-products" covers topics related to biodiesel quality, performance of combustion engines that use biodiesel and the emissions they generate. New routes to determinate biodiesel properties are proposed and the process how the raw material source, impurities and production practices can affect the quality of the biodiesel is analyzed. In relation to the utilization of biofuel, the performance of combustion engines fuelled by biodiesel and biodiesels blends are evaluated. The applications of glycerol, a byproduct of the biodiesel production process as a feedstock for biotechnological processes, and a key compound of the biorefinery of the future is also emphasized.

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