Analysis of the physicochemical properties of post-manufacturing waste derived from production of methyl esters from rapeseed oil

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A b s t r a c t. The technology of transesterification of biodiesel obtained from many agricultural products, which are often referred to as renewable resources, yields substantial amounts of by-products. They exhibit various properties that prompt scientific research into potential application thereof. Various spectroscopic methods, *e.g.* Fourier transform infrared spectroscopy, are being increasingly used in the research. In this paper, we present the results of Fourier transform infrared spectroscopy spectroscopy analyses of technical glycerine, distilled glycerine, and matter organic non glycerol, *i.e.* by-products of biodiesel production. To facilitate the spectroscopic analysis, a number of parameters were determined for all the materials, *e.g.* the calorific value, water content, sulphated ash content, methanol content, acidity, as well as the contents of esters, heavy metals, aldehydes, nitrogen, and phosphorus. The results indicate that the analysed products are characterised by a comparable calorific value in the range from 11.35 to 16.05 MJ kg^{-1} in the case of matter organic non glycerol and technical glycerine. Observation of changes in the position of selected peaks in the range of 3700-650 cm^{-1} in the Fourier transform infrared spectroscopy method facilitates determination of the level of degradation of the analysed material. Changes in the wavelength ranges can be used for monitoring the formation of secondary oxidation products containing carbonyl groups.

K e y w o r d s: technical glycerine, distilled glycerine, fatty acids, MONG, ATR-FTIR, calorific value, biodiesel, waste cooking oil

INTRODUCTION

The current problem of the greenhouse effect associated with emission of harmful compounds into the atmosphere has mobilised humans to search for alternative sources of energy that can offer a possibility of generation an addi-
tional income, also in rural areas. Hence, there is a growing demand for agricultural products (*e.g.* cereal, maize, or oilseeds) that can be utilised in production of renewable energy sources, *i.e.* biofuels, which are regarded as a form of technological progress towards reduction of greenhouse gas emissions, independence from fossil fuels, and general improvement of air quality (Jaecker-Voirol *et al.*, 2008; Norhasyimi *et al.,* 2010). The rapid development of biodiesel fuel industry has increased the availability of glycerine, which accounts for 10-20% of the total volume of biodiesel, *i.e.* as reported by Ayoub and Zuhairi (2012), approx. 4.53 kg of crude glycerol from 45.3 kg biodiesel (Melero *et al.*, 2008). In 2011, *ca.* 2 million kg of refined glycerine were produced on the market worldwide and *ca.* 2.6 million kg of this raw material were manufactured on the Brazilian market (FAPRI, 2015) Therefore, new applications of this raw material are still being developed. Its price has decreased as a result of increased production thereof, which also resulted in more than 2000 new industrial applications. For instance, it is used in many branches of industry utilising fatty acid derivatives, in medicinal and cosmetic products, food stuffs, feed, tobacco, paper, and textile products with excellent properties (elasticity and inherent stain resistance, low static generation), and in synthesis of biofuels, *i.e.* biodiesel, biohydrogen, or bioethanol *etc*. (Donkin *et al.,* 2009; Françozo *et al.,* 2013; Lawong and Shuriyapha, 2012). Despite this broad spectrum of

application of glycerine and its derivatives, the material is still considered as a waste product, which arouses concerns about its social and environmental impacts.

Besides biofuel, technical glycerine (often referred to as the glycerine phase) is one of the first products manufactured in the transesterification process. It contains up to 95% of glycerine and proportional amounts of water, sulphated ash, methanol, and matter organic non glycerol (MONG), with their final proportion determined by the composition of the input and output material and parameters of the transesterification process. Other methods for glycerol production involve anaerobic fermentation or chemical synthesis from other raw materials, which can be recovered as a by-product of soap or fat production (Quispe *et al.,* 2013; Yazdani and Gonzales, 2007).

The term 'glycerol' is only used to denote the pure chemical compound 1,2,3-propanetriol, whereas the term 'glycerine' refers to purified commercial products with glycerol content exceeding 95%. The products differ slightly in the glycerine content and such properties as odour, colour, or amounts of heavy metal, ester, or aldehyde impurities (Appleby *et al.,* 2005). Glycerine is soluble in many substances, *e.g.* alcohol or ethylene glycol, and partially insoluble in superior alcohol, fatty acids, and hydrocarbonate as well as in chlorinated solvents such as hexane, benzene, and chloroform. It is obtained by removal of salts, methanol, and free fatty acids. Pure glycerine is a non-toxic, non-irritating, biodegradable, and recyclable liquid. It is characterised by high stability in typical storage conditions, which is compatible with other chemicals. These properties allow application thereof as a humectant, plasticiser, skin emollient, thickener, and lubricant as well as a sweetening, thickening, and anti-freeze agent (Wolfson *et al.,* 2009). Matter organic non glycerol (MONG) is a by-product of glycerine production; the compound contains *ca.* 60% glycerine, sulphate ash, nitrogen, and phosphorus (Kachel-Jakubowska and Niedziółka, 2014). However, it does not contain hazardous substances

The application of technical glycerine or MONG as a fuel in industrial processes has many advantages, but there are some difficulties in the process of combustion thereof (Bohon *et al.,* 2011). Both products can also be a good raw material or additive in production of pellets (Kachel-Jakubowska *et al.,* 2011), possibly in combination with a binding agent (glycerine or MONG binder) improving the quality of the end product. They are characterised by a low calorific value, high auto-ignition temperature of *ca.* 370°C, in comparison with that of petrol (280°C) and kerosene (210°C), and high viscosity at room temperature. Combustion of these raw materials leads to formation of nitrogen oxides and carbon dioxide (CO_2), *i.e.* the major greenhouse gases (Gemma Vicente and Aracil, 2007).

Due to the presence of usually large amounts of impurities, glycerine contained in the glycerine layer should be purified prior to further use. The great numbers of requirements that have to be met by pharmaceutical, cosmetic, and edible glycerine necessitate application of techniques for processing the glycerine phase waste into glycerine that can satisfy customers requirements. The purity of crude catalytic glycerol depends on the process applied, *i.e.* the types of the catalyst and alcohol and the course of the reaction (Bournay *et al.,* 2005). This involves the use of devices facilitating the distillation process, which increases energy consumption in production of the analysed raw material.

Spectroscopic methods, including ATR-FTIR (Mueller *et al.,* 2013), provide an alternative solution for qualitative and quantitative analysis of solids, liquids, and gel samples, *i.e.* edible oil fats, and facilitate chemical characteristics of the samples (Hernandez-Martinez *et al.,* 2010; Pinto *et al.,* 2010). The advantage of the spectroscopic methods is the fact that they ensure analysis of very small samples in the range of several tens of microliters and minimise or even do not necessitate the sample preparation stage (Li-Chan *et al.,* 2010). Furthermore, spectroscopic methods, in particular ATR-FTIR spectroscopy, are being increasingly used for analysis of the composition and quality of raw materials. Samples are placed on a Ge-crystal and heated at a defined temperature, which substantially increases the rate of oxidation of the product (Pinto *et al.,* 2010).

The aim of this study was to present the physicochemical parameters of post-production raw materials derived from production of biofuels with the use of rapeseed oil as a raw material and to determine their potential to be used as separate or additional components of renewable biofuels. The investigations were divided into two parts. In the first part, the material was analysed for its density, calorific value, and chemical composition by determination of *e.g.* the fatty acid content. In the second stage of the research, the material was subjected to ATR-FTIR spectroscopy analysis.

MATERIALS AND METHODS

The study material consisted of samples placed in three 3 l containers; one of them contained technical glycerine, the second one - a product derived in the process of purification of technical glycerine, commonly referred to as MONG, and the third container comprised pure pharmaceutical (distilled) glycerine. The raw material was part of a production batch of rapeseed oil biofuel produced in Trzebinia S.A. Refinery in 2015.

The analysis of the basic composition of the technical and pharmaceutical glycerine as well as MONG in terms of the content of individual components was performed in accordance with the applicable standards: colour – ISO 2211; content of glycerine, sulphated ash, and water, refractive index, chloride content, acidity, halogen content, contents of esters, sugar, heavy metals, and aldehydes – Eur.Ph.2005:496; methanol content – PN-EN 14110:2004; MONG content – WT 93/2009. The analyses were carried out in a laboratory at ENL Ekonaft Sp. z o.o. The content

of fatty acids was determined in accordance with standard PN-EN ISO 5508:1996 – animal and vegetable fats and oils – analysis of methyl esters of fatty acids by gas chromatography at the Central Agroecological Laboratory, University of Life Sciences in Lublin.

The analysis of the density of the samples was carried out with a portable laboratory densitometer DM-340 series Den-Di (LEMIS INSTRUMENTS AS LEMIS Baltic Lithuania) used in petrochemical, chemical, and pharmaceutical industries. The calorific value was determined using an automatic isoperibol calorimeter Parr 6400 (from Parr Instrument Company, USA) in accordance with standard PN-EN 14918:2010. The measurement consisted in complete combustion of a 2 g (±0.0002 g) sample of the analysed product in an oxygen atmosphere under a pressure of 3 MPa in a bomb calorimeter immersed in water.

The measurements of ATR-FTIR background-corrected spectra were carried out in solvents using a HATR Getrough (45° cut, yielding 10 internal reflections) crystal plate for liquids and recorded with a VERTEX 70 Fourier transform infrared spectrometer (Bruker, USA). Typically, 25 scans were collected, Fourier-transformed, and averaged for each measurement (10 spectra were obtained and averaged for each sample). The IR absorption spectra at a resolution of one data point per 1 cm^{-1} were obtained in the region between 4000 and 400 cm^{-1}. The instrument was purged with argon for 40 min before and during the measurements. The Ge crystal was cleaned with ultra-pure solvents *e.g.* methanol, propan-2-ol, and ethanol (Sigma-Aldrich Co.). The samples were deposited on a Ge crystal and the measurement was performed in N_2 atmosphere. All experiments were carried out at 23°C.

The results of the calorific value and density of the examined products were analysed statistically taking into account the mean value, ± standard deviation, and post-hoc Tukey test at a significance level of $p < 0.05$ with the use of Statistica 10 (StatSoft, Inc., USA) software.

RESULTS AND DISCUSSION

Table 1 shows basic results of the physicochemical properties of the examined material. Technical glycerine was characterised by the highest calorific value (16.051 MJ kg^{-1}), which can probably be explained by the low content of methanol (0.15% m m^{-1}). MONG, for which the methanol content is not determined in laboratories, following an assumption of low or zero amounts of the compound,

T a b l e 1. Physicochemical properties of the by-products of production of the analysed biofuels

Parameter	Unit	Technical glycerine	Pharmaceutical glycerine	MONG
Calorific value	MJ kg^{-1}	16.051±0.029a	13.491±0.006b	11.349±0.005c
Density	kg cm^{-3}	1283±1.52a	1264±1.52a	1289±2.08a
Glycerine content	% m m^{-1}	91.02a	99.90b	55c
Water content	% m m^{-1}	3.65	0.10	-
Sulphated ash content	% m m^{-1}	3.54	0.00	21.7
Methanol content	% m m^{-1}	0.15	–	–
MONG content	% m m^{-1}	1.64	–	–
Colour	APHA	–	1	–
Refractive index	–	–	1.472	–
Acidity	0.1M NaOH in ml	–	0.12	–
Chlorides	ppm	–	>5	–
Halogen content	ppm	–	>35	–
Ester content	0.1 M HCl in ml	–	8.6	–
Heavy metal content	ppm	–	>5	–
Aldehyde content	ppm	–	>5	–
Nitrogen content	ppm	–	–	1042
Phosphorus content	ppm	–	–	7600

a, b, c – average values marked with the same letter are not statistically significantly different $p < 0.05$.

exhibited the lowest value (11.349 MJ kg^{-1}). As indicated by other reports, glycerine is characterised by moderate calorific values ranging from 16.07 to 19.2 MJ kg^{-1}, and it is still not considered as a suitable fuel product (Bohon *et al.*, 2011; Lima da Silva and Mueller, 2010; Niedziółka and Zuchniarz, 2007). The results obtained are comparable with those reported for agricultural plant biomass, *i.e.* from 15 to 17 MJ kg^{-1} for wet biomass or up to 19 MJ kg^{-1} for completely dried biomass (Dharmadi *et al.*, 2006; Niedziółka *et al.*, 2015). The highest density was noted for MONG (1 289 kg m^{-3}) and the lowest was exhibited by the pharmaceutical glycerine (1 264 kg m^{-3}). The results obtained can also be compared to those reported by other researchers, *i.e.* 1260-1261 kg m^{-3} (Saifuddin *et al.*, 2014). The other results presented in Table 1, *e.g.* the contents of water and sulphated ash, represented the lower limits specified in the requirement of their standards. The statistical analysis based on post-hoc Tukey test at a significance level of $p < 0.05$ confirmed the statistically significant differences in the calorific values between the by-products of biofuel production. No statistically significant differences were noted for the density of glycerine and MONG.

Since glycerine is a derivative of raw materials with a broad spectrum of fatty acids and since there are no available publications, their content was determined in the examined glycerine and MONG samples. The probable content of these compounds in the analysed samples can have a significant effect on their oxidative degradation during the storage period (Table 2).

T a b l e 2. Fatty acid content in technical glycerine, pharmaceutical glycerine, and MONG

Parameter	Technical glycerine (%)	Pharmaceutical glycerine (%)	MONG (%)
C10:0	4.18 ± 0.04	–	–
C11:0	0.90 ± 0.05	–	–
C12:0	1.09 ± 0.08	–	–
C13:0	4.40 ± 0.21	–	–
C14:0	9.18 ± 0.30	–	4.14
C14:1	5.58 ± 0.04	–	3.56 ± 0.48
C15:0	28.74 ± 0.69	–	12.53 ± 1.72
C16:0	5.75 ± 0.46	100	12.68 ± 0.82
C17:0	1.44 ± 0.23	–	–
C18:0	37.71 ± 0.76	–	67.10 ± 1.37
SFA	94.42	100	96.45
MUFA	5.58	–	3.56

SFA – saturated fatty acids, MUFA – monounsaturated fatty acids.

Decomposition products, which are relevant in terms of application, can have an adverse effect on the odour or nutritional value of biofuels. The results obtained indicate that the technical glycerine, *i.e.* one of the primary products of separation of the glycerine fraction from biodiesel rapeseed methyl ester (RME), is characterised by the greatest spectrum of fatty acids. Ten fatty acids were identified in the technical glycerine. The largest group of the main fatty acids was composed of fatty acids characterised by over 1% content: decanoic acid (C10:0), n-dodecanoic acid (C12:0), tridecanoic acid (C13:0), tetradecanoic acid C(14:0), cis-9-tetradecanoic acid C(14:1), pentadecanoic acid (C15:0), hexadecanoic acid (C16:0), and octadecanoic acid (C18:0). Over 90% of the fatty acid composition was represented by saturated fatty acids (SFAs). The analysis of MONG revealed similar contents of SFAs: tetradecanoic acid (C14:0), pentadecanoic acid (C15:0), hexadecanoic acid (C16:0), octadecanoic acid (C18:0), and MUFA – cis-9-tetradecanoic acid (C14:1). The pharmaceutical glycerine was composed of 100% of palmitic acid (C16:0), *i.e.* hexadecanoic acid from the group of saturated fatty acids. The differences in the fatty acid content may be explained by the fact that these industrial products may have originated from different production batches or the raw material may have been sampled from each container at different time points. The other fraction of the samples contained MUFAs, *i.e.* monounsaturated fatty acids, represented by myristoleic acid.

Figure 1 presents ATR-FTIR spectra of the analysed samples of technical glycerine – Panel A, distilled glycerine – Panel B, and MONG – Panel C. Infrared spectroscopy measurements provide information about the purity of the analysed compound, which can be used as biodiesel or a food additive (Mahamuni and Adewuyi, 2009; Saifuddin *et al.*, 2014). It should be emphasised that infrared spectroscopy methods are more frequently used by researchers for evaluation of the quality of biofuels (Mueller *et al.*, 2013; Sahoo *et al.*, 2012; Valerio *et al.*, 2015). In ATR-FTIR spectroscopy, there are characteristic regions that undeniably describe vibrations of functional groups indicating both the quality of a product (Matwijczuk *et al.*, 2015; Saifuddin and Refal, 2014; Valerio *et al.*, 2015) and the molecular interactions of compounds and additives contained therein. All the analysed compounds are characterised by a very clear infrared spectrum, which largely facilitates analysis and interpretation thereof. At a maximum centred at *ca*. 1 721 cm^{-1}, a band originating from the C=O group can be seen (Matwijczuk *et al.*, 2015; Yang *et al.*, 2012) only in the MONG samples, whereas it is completely invisible in the case of the technical and distilled glycerine. In the case of MONG, the band exhibits very weak intensity, which may indicate the presence of a small amount of various impurities in the analysed sample. Various impurities present in technical glycerine, distilled glycerine, or MONG can originate to a greater or lesser
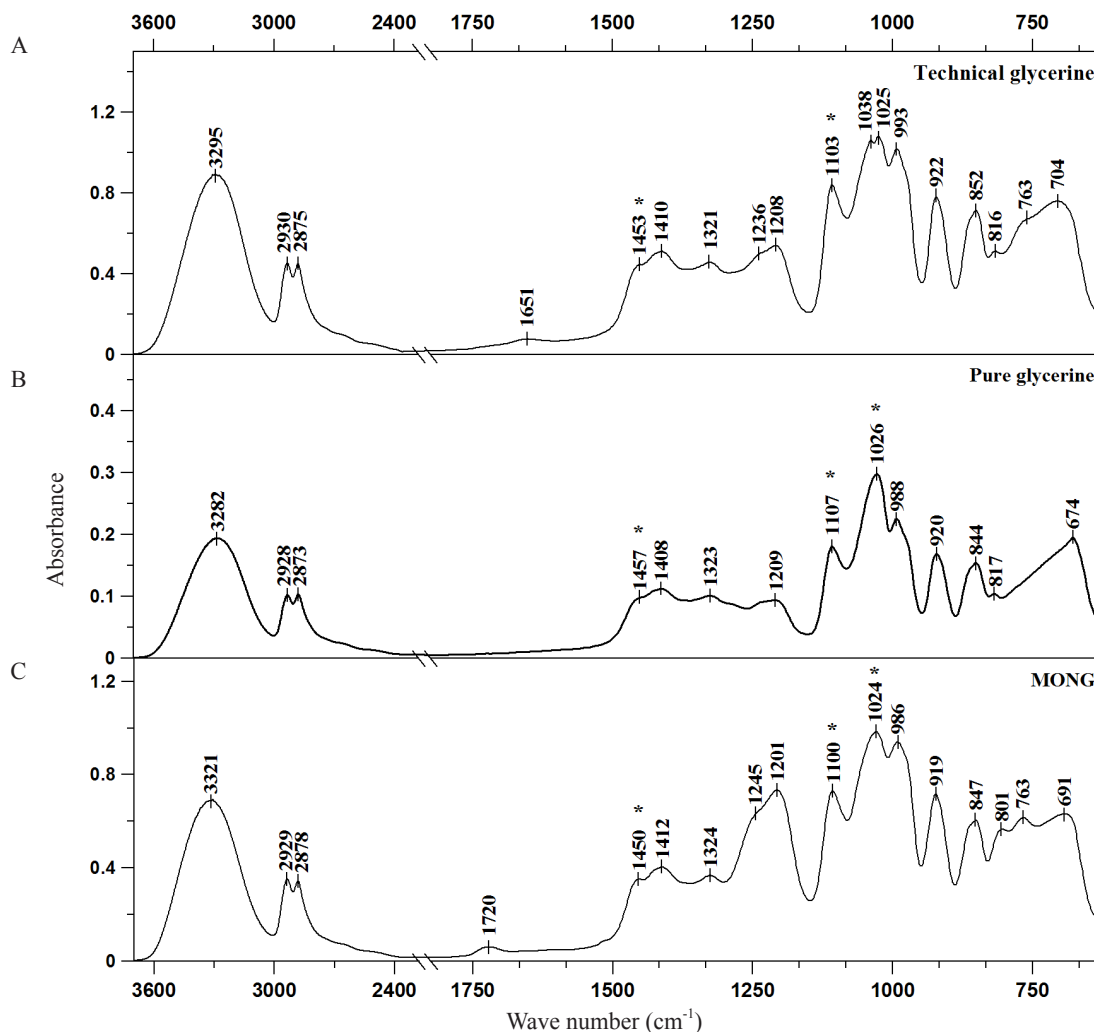
Fig. 1. ATR-FTIR absorption spectra for: A – technical glycerine, B – pharmaceutical glycerine, and C – MONG. The measurements were performed at a temperature of 23°C. The asterisk symbol denotes both the solvent and molecule band.

extent from the processes of purification of the products (Yang *et al.,* 2012); they include *e.g.* small amounts of methanol and water or other post-manufacturing wastes (Valerio *et al.,* 2015). The vibrations from the 3 000-3 600 cm^{-1} region with a maximum at *ca.* 3 300 cm^{-1} (visible for all the tested samples) should be attributed mainly to stretching vibrations of the –OH groups in the water molecules and also in the glycerine molecules. This implies low content of H$_2$O in the analysed materials (low H$_2$O content in a sample may be related to the lower level of purification thereof) (Valerio *et al.,* 2015). Noteworthy, there are evident changes in the intensity in the spectrum from the aforementioned region; the intensity of the distilled glycerine band is nearly four-fold lower than that of the corresponding band for the technical glycerine. These changes should obviously be attributed to the considerably higher degree of purification of the product; the intensity of this band in the case of MONG accounts for approx. 80% of the corresponding band in the technical glycerine spectrum (Valerio *et al.,* 2015) (Fig. 1, Table 3). Another

characteristic region that is similar in all the analysed spectra is the 2 700-3 000 cm^{-1} vibration region characteristic for both symmetrical and asymmetrical vibrations of the -CH$_2$ and -CH$_3$ groups (Mahamuni and Adewuyi, 2009).

In turn, the band with a maximum at 1 651 cm^{-1}, which is visible only in the technical glycerine (very weakly in MONG), should be attributed to the stretching vibrations of the C=C group (as well as C=O). Another three bands with a maximum at *ca.* 1 450, 1 410, and 1 320 cm^{-1} (exact positions of the maxima, Fig. 1 and Table 3) should be ascribed to stretching and deformation vibrations of the –C-H groups in a given type of the product (in the glycerine molecule). These bands also specifically identify the degree of purity/purification of the product (Mahamuni and Adewuyi, 2009).

The vibrations of these groups (with a maximum at *ca.* 1 450, 1 410, and 1 320 cm^{-1}) are highly similar in all the analysed samples; hence, their analytical value is low. However, the spectra of distilled glycerine have substantially lower intensity in comparison with the other

T a b l e 3. Position of the maxima of absorption bands assigned to appropriate vibrations for the potential biofuels analysed (technical glycerine, pharmaceutical glycerine, and MONG) in the spectral range of 3700-650 cm^{-1}

FTIR			
Position of bands (cm^{-1})			Type and origin of vibrations
Technical glycerine	Pharmaceutical glycerine	MONG	
3295st	3282w	3321m	ν (O-H) in H$_2$O or in glycerine
2930	2928	2929	CH$_{2, s+as}$, CH$_{3, s+as}$ aliphatic group of triglycerides
2875	2873	2878	
–	–	1720	C=O group of Ester
1651	–	–	ν(C=C)
1453	1457	1450	-C-H (in CH$_2$) bending
1410	1408	1412	=C-H (cis-) bending
1321	1323	1324	δ(CH)
1236	1237	1245	C-O stretching or -O-CH$_2$-C
1208m	1209w	1201s	ν(C-O) in Ester group
1103	1107	1100	ν(C-C) + ν(C-O-C)$_{as}$
1038	–	–	δ(CH) + ν(C-C)
1025	1026	1024	
993	988	986	ν(C-C)
922	920	919	-OH (in glyceryne)
852	844	847	ν(C-O-C)$_s$
816	817	801	ν(C-O-C)$_s$ or ν(C-C)$_s$
763	-	763	ν(C-C) + ν(C=C)
704	674	691	-CH$_2$- rocking

ν – stretching vibrations, δ – deformation vibrations, s – symmetric, as – asymmetric, st – strong, w – weak, m – medium.

samples, as in the case of the stretching bands of the –OH group presented above, which clearly indicates a high degree of purification and many potential applications of the end product (Mahamuni and Adewuyi, 2009).

Another very characteristic region, which is a specific fingerprint in investigations of various esters, is associated with the vibrations at the 1 000-1 300 cm^{-1} wavelength range. Many differences can be noted in this region, which constitutes a very good analytical area (Sahoo *et al.,* 2012). The two characteristic bands appearing at 1 208 and 1 236 cm^{-1} for the technical glycerine, 1 209 cm^{-1} for the distilled glycerine, and 1 201 and 1 245 cm^{-1} for MONG are characteristic for stretching vibrations of the C-O groups (in the C-O-C ester group) (Saifuddin and Refal, 2014). The lowest intensity of these bands is noted for the distilled glycerine, which confirms previous observations of the purity of the compound and indicates a higher

degree of purification of the product. The greatest intensity accompanied by substantial broadening of these bands was noted in the case of MONG. The band with a maximum at *ca*. 1 100 cm^{-1} present in all the analysed samples should be associated with the stretching vibrations of the C-C groups or (as already mentioned) the asymmetric vibrations of the C-O-Cgroup (Rabelo *et al.,* 2015). Vibrations from the 1 050-1 000 cm^{-1} region, which should be attributed to the deformation vibrations of the C-H group and the stretching vibrations of the C-C group, indicate relatively distinct changes in the analysed samples. There are two clear bands with a maximum at *ca*. 1 038 and 1 025 cm^{-1} in the case of the technical glycerine and only one band for the techni-cal glycerine and MONG with a maximum at 1 026 and 1 024 cm^{-1}, respectively. The intensity of this area declines with the decrease in the methanol content in the analysed esters, and the lowest intensity is shown in the case of the

distilled glycerine. Another three very similar bands from the region from 1 000 to 830 cm⁻¹ in all the samples are characteristic for C-C and -OH stretching vibrations in glycerine molecules and C-O-C symmetrical vibrations (Rabelo *et al.,* 2015).

The analytically available region at 820-660 cm⁻¹ shows several differences in the band vibrations. The vibrations with a maximum at 816 (technical glycerine), 817 (distilled glycerine), and 801 cm⁻¹ (MONG) should be attributed to C-O-C or C-C stretching vibrations; they are highly similar in all the analysed samples. In turn, in the distilled glycerine, there is no clear band at *ca*. 763 cm⁻¹ characteristic for C-C and C=C vibrations, which is distinctly visible in the technical glycerine and MONG; this can be related to the fact that these substances remain in the waste produced during purification of technical glycerine. The last vibrations characteristic for the CH_2 group are noted at: 704, 674, and 691 cm⁻¹, technical glycerine, distilled glycerine, MONG, respectively. All the above-described bands are presented in detail in Table 3.

CONCLUSIONS

1. The investigation results obtained for these products have confirmed their wide spectrum of technical industry applications. The quantitative and qualitative analyses of *e.g.* the calorific value have revealed that the biofuels do not differ markedly from other products that are referred to as renewable energy sources, such as pellets.

2. During the analysis of the spectra obtained with the ATR-FTIR infrared spectroscopy, relevant spectral regions that can provide readily available information about the applicability of the investigated products in the technical and food industries were examined.

3. A very important finding of the spectroscopic analyses presented in this article is the possibility of performing a time- and cost-efficient ATR-FTIR infrared spectroscopy analysis of the quality of products that can potentially be used in food industry.

4. The infrared spectroscopy analyses revealed distinct bands, which clearly indicated the quality of the products (mainly bands with a maximum at 1 720, 1 651 cm⁻¹ as well as bands from the range of 1 220-1 250 cm⁻¹).

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