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Quality of rapeseed bio-fuel waste: optical properties

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A b s t r a c t. The objective of the presented work was to examine the optical properties of selected bio-fuel waste. Three independent optical methods: UV-Vis spectroscopy, infrared spectroscopy and chromametric measurements were applied to establish the possible quality control test for the obtained substances. The following by-products were tested: distilled glycerine, technical glycerine and matter organic non glycerine fraction from rapeseed oil bio-fuel production. The results show that analysis of UV-Vis spectra can give rapid information about the purity of distilled glycerine, while no direct information can be obtained concerning the concentration and kind of impurities. Transmission mode is more useful as compared to absorption, concerning the detection abilities of average UV-Vis spectrometers. Infrared spectroscopy can be used as a complementary method for determining impurities/admixtures in samples. Measurements of chroma give the quickest data to compare the colour of biofuel by-products obtained by different producers. The condition is, however, that the products are received through the same or similar chemical processes. The other important factor is application of well defined measuring background. All the discussed analyses are quick, cheap and non-destructive, and can help to compare the quality of products.

K e y w o r d s: rapeseed bio-fuel, waste, optical spectroscopy, infrared absorption, colour

INTRODUCTION

Bio-fuel waste management is one of the most concerning matters in the developing chemical industry. It is becoming more important for biodiesel producers to increase revenues by selling by-product of glycerol as well as finding use for other by-products. Purified glycerol has found many applications such as a substrate for chemical synthesis (Alavi Nijke, 2007; Aresta *et al*., 2009; Kim *et al*., 2007 Wolfson and Dlugy, 2007), bioconversion (Chen *et al*., 2002; Kim *et al*., 2007; Nicol *et al*., 2012), substrate for food and cosmetic industry, production of surfactants (Jurado *et al*., 2012; Urata and Takaishi, 2002; Xu *et al*., 2011), production of biodegradable packaging (Liu *et al*., 2001), application in freezing (Izawa *et al*., 2004) or as a medium in medical care (Gwon *et al*., 2009; Nho *et al*., 2009). Other by-products such as crude glycerine or MONG fraction are not frequently reported in literature, their basic physico-chemical properties are not described, there is no data on their possible application. Yet, commercial comparison of an individual fraction of waste is problematic, mainly because of different bio-fuel production techniques (Anez-Lingerfelt, 2009). Therefore, the objective is to find a non-destructive, quick and cheap method for analysis of the properties of these by-products to avoid expensive and time consuming chemical analyses. The basic and easily observable parameter is the different colour of fractions received by individual producers, often described as transparent, through shades of yellow to dark brown.

Different spectroscopy techniques have already been applied by the producers of synthetic glycerol to study its purity (Brodina and Rösslerb, 2005; Dow Performance Materials, 2012; Mudaligne *et al*., 2007). Unfortunately, to date, no spectroscopic data exist on the optical parameters of other bio-fuel waste.

The aim of the presented work was to evaluate the optical properties of three rapeseed oil bio-fuel production wastes: distilled glycerine (DG), technical glycerine (TG) and matter organic non glycerine fraction (MONG fraction). Three independent methods were applied: UV-Vis spectroscopy, infrared spectroscopy and colorimetric measurements.

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MATERIAL AND METHODS

Experimental material originated from Trzebinia Refinery S.A. Five-litre non-transparent and air tight barrels contained three different by-products from rapeseed oil biofuel production. Analyzed samples were:
– distilled glycerine (DG),
– technical glycerine (TG),
– matter organic non glycerine fraction (MONG).

The MONG fraction contains usually mono-, di- and triglycerides as well as methyl esters and other organics. A detailed description of the processes leading to the production of the individual fractions is to be found in the internal technical standard protocols of Trzebinia Refinery S.A.

Measurements of the optical properties of the samples:
– measurements of absorption/transmission spectra in the UV-Vis range (280-800 nm) were performed with the usage of double beam Varian Carry Bio 300 spectrophotometer. Empty measuring quartz cuvettes cleaned with organic solvents were used as the baseline. All the measurements were conducted at 20±1°C.
– Infrared absorption spectra were recorded with the Bruker Vector 33 Fourier-transform infrared absorption spectrometer equipped with the attenuated total reflection set-up (ATR-FTIR). Clean ATR ZnSe crystal element (45° cut) yielding 10 internal reflections was used as a background. The instrument was purged with argon for 40 min prior to and continuously during the measurements. Samples were deposited directly on the crystal. Absorption spectra at a resolution of one data point every 2 cm^{-1} were obtained in the region between 4 000 and 400 cm^{-1}. Typically, 10 scans were collected, Fourier-transformed and averaged for each measurement. All experiments were done at 20±1°C. Spectral analysis was performed with OPUS software (Bruker, Germany).
– Colorimetric measurements were obtained by the use of a Minolta CR-221 (Minolta, Osaka, Japan) chroma meter, with 45° circumferential illumination and 0° viewing angle geometry measurement system, aperture size ∅3 mm and D65 light source (pulsed xenon lamp).

The CIE *Lab* (CIE $L^*a^*b^*$) colour scale specified by the International Commission on Illumination (Commission Internationale de l'Éclairage, CIE) was applied. The coordinates of CIE Lab evaluation system represent: the luminosity L^* (0 for black and 100 for white), chromaticity a^* on a green (negative values) to red/magenta (positive values) axis, and chromaticity b^* on a blue (negative values) to yellow (positive values) axis.

The colour parameters were measured without any pretreatment operations, such as sample extraction or centrifugation. Prior to analysis all samples were left for 2 h to equilibrate at room temperature and the instrument was calibrated to a white ceramic tile (CIE $L^* = 99.25$; $a^* = -0.60$; $b^* = 1.87$) according to the manufacturer recommendations. Standard 10 mm optical path length polypropylene cuvettes were filled with 4 ml of specimens. Cuvettes were covered from three sides, except the one facing the chroma meter measuring head, with a cardboard to provide a black or white background. Measurements were performed in darkened room to exclude external light sources. The chroma meter automatically generated 3 measurements from which it calculated a mean colour measurement. To ensure the instrument accurate repeatability of measurement, colour coordinates were recorded fivefold for each sample and the mean $L^*a^*b^*$ values were calculated. The colorimetric measurements of both backgrounds were taken under identical conditions, using a blank cuvette and an appropriate background cardboard.

From the given CIE Lab coordinates, the following chroma parameters were calculated:

Hue angle:

$$h = \arctan\left(\frac{b^*}{a^*}\right). \quad (1)$$

Chroma C^*, which indicates saturation of colour *ie* the proportion in which the colour is mixed with white, black or grey (Brainard, 2003):

$$C^* = \sqrt{a^{*2} + b^{*2}}. \quad (2)$$

Distance between two samples or distance from background:

$$\Delta E_{12} = \sqrt{(L_1^* - L_2^*)^2 + (a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2}. \quad (3)$$

Analytical grade commercial glycerol (CG) (POCH Gliwice, Poland) was used as an external reference.

To evaluate the differences in colour variation values between the tested specimens, data were statistically analyzed with analysis of variance (ANOVA) at the $p<0.05$ significance level with Statistica software (version 10, StatSoft Inc., Tulsa, OK, USA), followed by Bonferroni all-pair wise analysis to determine the differences among the samples.

RESULTS AND DISCUSSION

Figure 1 shows typical measured UV-Vis spectra of rape oil biofuel by-products (absorption spectra (Fig. 1a), transmission spectra (Fig. 1b); 1 – DG, 2 – TG, 3 – MONG fraction). Absorbance is a measure of the quantity of light that a sample neither transmits nor reflects and is proportional to the concentration of a substance (depending on a chromophore) and the size of its particles. Usually, colour substances reveal characteristic spectral features in this region. Unfortunately, none of the examined by-products has characteristic absorbance peaks in UV-Vis region. Under the applied experimental setup it was not possible to measure the absorption spectrum of the MONG fraction as the absorption from 300 to 600 nm exceeded 8 arbitral units which is the measurement limit of the instrument used. The spectrum of technical glycerine at the range below 400 nm cannot be considered for the same reason.

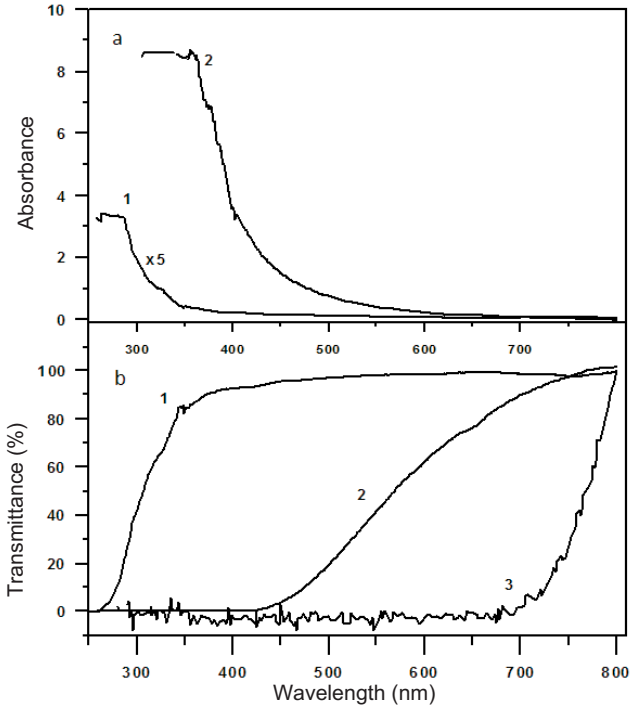

Fig. 1. UV-Vis spectra of rapeseed oil bio-fuel production waste: a – absorbance, b – transmittance; 1 – DG, 2 – TG, 3 – MONG fraction.

Although TG has a visible yellow colour, this feature is not clearly revealed in the absorption spectrum. Both spectra of distilled glycerine and technical glycerine show the typical light scattering shape depending on the size of the examined molecules (Castanho *et al*., 1997). Higher scattering in the case of the technical glycerine indicates its contamination with other substances.

Typically, absorbance ranges from 0 to 1, but it can go higher depending on the detection qualities of the spectrophotometer used. Unfortunately, for certain wavelengths the information obtained may be not accurate due to the measuring conditions. In our case the absorbance level of distilled glycerine at 290 nm amounts to *ca* 0.6, which means 4-fold weakening of the incident light. Although from the theoretical point of view it is a desirable value, the wavelength of 290 nm is the wavelength limit of the spectrophotometer applied in the absorbance mode. Similarly, the absorbance level of *ca* 8 units is a limiting value at the wavelength of 370 nm.

Therefore, measurements in transmittance mode are recommended. The transmittance of a sample is the ratio of the intensity of the light that has passed through the sample to the intensity of the light when it entered the sample (T = I*out*/I*in*). The transmittance is displayed as a percentage on the top scale of the meter. As seen from the spectra in the lower panel, distilled glycerine transmits light at the whole measurement range while technical glycerine lets through the light above 450 nm. UV-Vis transmission spectra are used by the commercial producers to estimate the level of impurities of their products. As seen from the transmittance spectrum having the characteristic features in the spectral region between 250 and 350 nm, glycerine obtained in the process of distillation reveals a high level of impurities (Dow Performance Materials, 2012). MONG fraction is practically non-transparent for wavelengths shorter than 700 nm.

Figure 2 shows typical infrared absorbance spectra of the examined rape oil bio-fuel by-products in the spectral range between 3 800 and 2 400 cm^{-1}. For each sample spectra were normalized at their absorbance maximum representing OH (C-OH) group stretching vibration. The main spectral features are the bands corresponding to anti-symmetric and symmetric stretching vibrations in the CH_2 groups at 2 932 and 2 877 cm^{-1}, respectively, and the broad band representing OH (C-OH) group stretching vibration with the maximum at *ca* 3 200-3 300 nm. The registered spectra are

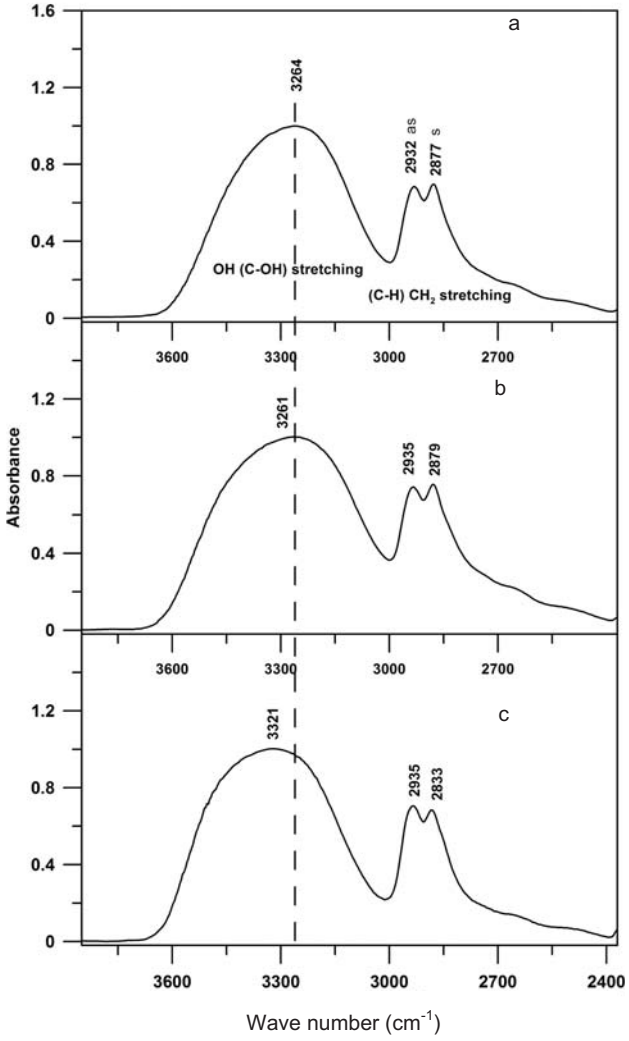

Fig. 2. FTIR – ATR spectra of rapeseed oil bio-fuel production waste in the spectral region between 3 800 and 2 400 cm^{-1}: a – DG, b – TG, c – MONG fraction.

in agreement with those previously published for commercial glycerine and crude glycerine at ambient pH (Kongjao *et al*., 2010). Despite the fact that MONG fraction consists mainly of organic matter (oil depleted from glycerol, ash and water), it has the same functional groups as glycerol. Therefore, its FTIR spectra registered in the above mentioned region are similar. As seen from the spectra, this band in the MONG fraction is shifted towards higher wave number by *ca* 60 cm^{-1} as compared to the sample containing distilled glycerine. Another interesting feature is the explicit difference in respective intensity of the bands representing CH_2 and CH stretching vibrations.

Figure 3 shows typical results of FTIR infrared absorbance spectra measurements of the rapeseed oil bio-fuel by-products in the spectral range between 1800 and 600 cm^{-1}. Spectra were normalized at the maximum absorbance representing OH group stretching vibration (at *ca* 3 260 cm^{-1}, beyond the wave number range shown on this figure). The main spectral features of all the measured spectra are the bands corresponding to anti-symmetric and symmetric stretching vibrations in the C-O group at 1 208, 1 107 and 1 028 cm^{-1}, CH_2 scissoring vibration at 1 456 cm^{-1}, CH_2 bending at 1 412 cm^{-1}, =CH bending out of plane of the molecule (δ_{oop}) at *ca* 850 and 669 cm^{-1} and OH bending at 1 327 cm^{-1}. The registered spectra differ by the intensities the of registered bands. The set of the strong bands characteristic of C-O and COO- group stretching vibrations and C-OH bending in the spectral region between 900 and 1 100 not observed for commercial glycerol (Kongjao *et al*., 2010) indicate possible contamination of the sample with the remains of alcohol (Georgiev *et al*., 2007).

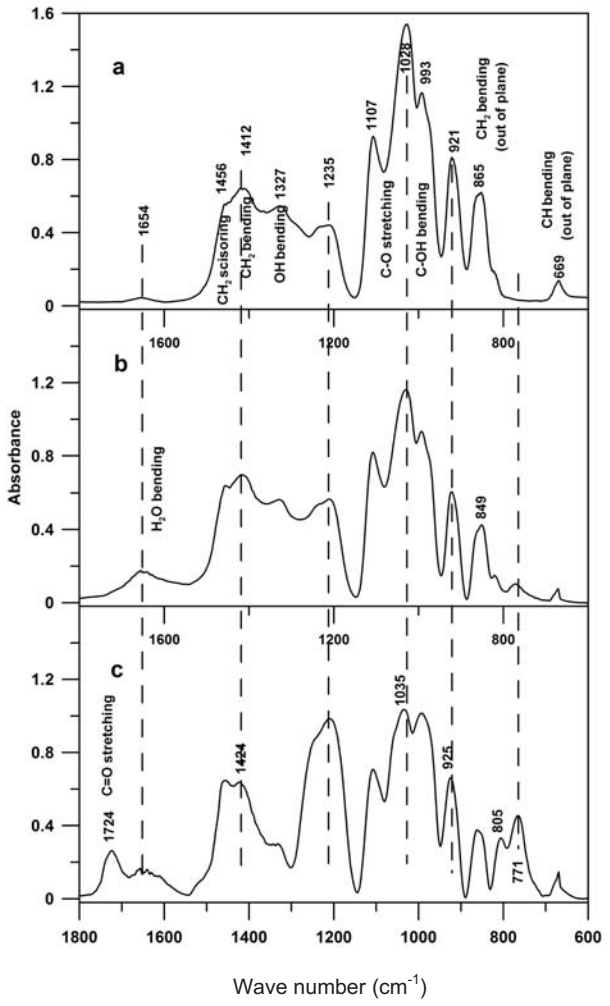

Fig. 3. FTIR – ATR spectra of rapeseed oil bio-fuel production waste in the spectral region between 1 800 and 600 cm^{-1}: a – DG, b – TG, c – MONG fraction. Characteristic vibrations as indicated.

Spectra of the distilled and technical glycerine differ only by the presence of an additional band at 771 cm^{-1}, representing most probably the =CH group bending mode in the latter sample. The spectrum of MONG fraction shows a relative decrease in the intensity of the band representing OH bending vibration, accompanied with the appearance of the band representing C=O stretching at 1 724 and strong C-O stretching at 1 208 cm^{-1}. An extra medium intensity band appears at 805 cm^{-1} and probably represents one of the -CH group bending modes.

As samples DG and TG are transparent in the visual spectral region (shown by the UV-Vis measurements), we decided to apply the chromametric technique of measuring colour at two different well defined backgrounds using analytical grade commercial glycerol as a reference. Basically a chroma difference is understood as a distance between two colours, typically two points in a coordinate system, in a predefined colour space. In some industries there is often a well defined and reproducible physical reference sample.

Table 1 shows the colour parameters represented in CIE $L^*a^*b^*$ colour space at different backgrounds. CIE $L^*a^*b^*$ coordinates represent the colour in the three dimensional colour space (for details see Materials and Methods section). Chroma C^* represents the saturation of the colour as compared to the main colour from the palette scheme, while hue angle h represents the colour shade.

As seen from Table 1, samples analytical grade commercial glycerine and distilled glycerine show similar parameters L^* and a^* but different values for b^*. This indicates that their luminosity and the colour on green-red a^* scale are similar, while the reference sample is bluish and sample DG is yellowish. Such a phenomenon may be clear indication of impurities in the distilled glycerine expressed only slightly by its UV-Vis and FTIR spectra, expressed mainly by the changes in the samples turbidity. It is not possible to tell the difference between these two samples from the straight visual observation which is also indicated by a small distance ΔE of the sample marked DG from the reference. Interestingly, visibly transparent and comparable high purity commercial glycerol as well as distilled glycerine show

T a b l e 1. Analysis of the colours of the samples of rapeseed oil bio-fuel production wastes according to the CIE *L*a*b** standards

Sample	CIE *L*a*b** coordinate			Hue angle	Chroma	Distance from	
	*L**	*a**	*b**	*h*	*C**	background ΔE_{bg}	reference sample 0 ΔE_{ref}
				White background			
CG	17.87 ± 0.04a	0.72 ± 0.03a	-2.77 ± 0.02a	-1.31 ± 0.01a	2.86 ± 0.03a	8.35 ± 0.09	–
DG	18.55 ± 0.04b	0.72 ± 0.07a	1.76 ± 0.05b	-1.18 ± 0.02b	1.90 ± 0.07b	9.20 ± 0.07	1.22 ± 0.08
TG	7.36 ± 0.04c	4.00 ± 0.04b	6.01 ± 0.05c	0.98 ± 0.01c	7.22 ± 0.02c	10.44 ± 0.03	14.06 ± 0.05
MONG	7.63 ± 0.04d	0.07 ± 0.01c	4.15 ± 0.08d	1.56 ± 0.01d	4.15 ± 0.08d	8.36 ± 0.011	12.38 ± 0.01
Background	9.62 ± 0.06	1.42 ± 0.11	-3.85 ± 0.03	-1.22 ± 0.02	4.11 ± 0.07	–	–
				Black background			
CG	5.28 ± 0.04a	0.21 ± 0.05a	-0.91 ± 0.03a	-1.34 ± 0.06ab	0.93 ± 0.02a	3.12 ± 0.15	–
DG	1.90 ± 0.06b	0.22 ± 0.06a	-0.83 ± 0.04b	-1.31 ± 0.06abc	0.86 ± 0.04a	0.51 ± 0.14	3.38 ± 0.09
TG	4.26 ± 0.03c	-0.43 ± 0.15b	0.98 ± 0.04c	-1.17 ± 0.12b	1.08 ± 0.09b	2.67 ± 0.19	2.25 ± 0.08
MONG	7.48 ± 0.03d	-0.46 ± 0.07b	4.50 ± 0.03d	-1.47 ± 0.02c	4.52 ± 0.03c	7.31 ± 0.16	5.87 ± 0.02
Background	2.12 ± 0.17	0.30 ± 0.14	-0.41 ± 0.05	-0.97 ± 0.20	0.52 ± 0.11	–	–

CG – analytical grade commercial glycerine, DG – distilled glycerine, TG – technical glycerine, MONG – matter organic non glycerine fraction. Data represent mean values of five replications and their standard deviations. Means with the same superscript letter in the same column for given background are not significantly different (all-pair wise Bonferronii t-test, $p<0.05$).

different colour parameters at both backgrounds. Technical glycerine shows different values for all the parameters as compared to the reference sample. It shows the highest colour saturation (chroma) and the highest parameter of shade (hue angle) at the white background which is consistent with its visible yellow colour. It also indicates a huge ΔE difference. Relatively high chroma but lower hue angle in the case of MONG fraction indicate its lower saturation with the colour from the colour palette but also a much darker shade. The observed ΔE strongly depends on the background. In the case of white background it works well with bright and transparent samples, such as analyzed destilled and technical glycerine.

CONCLUSIONS

1. UV-Vis spectra of the distilled glycerine from rapeseed oil bio-fuel production waste can give rapid information about its purity. In the case of technical glycerine and MONG fraction the measurements in transmittance mode are recommended due to high absorbance level of such a samples. No direct information can be obtained concerning the concentration and kind of impurities in these fractions. The measurements in transmittance mode are recommended due to a high absorbance level of such a samples.

2. FTIR spectra can be used as a complementary method for determining samples impurities or admixtures.

3. Measurements of chroma in the CIE *Lab L*a*b** scale can give the quickest data to compare the colour of biofuel by-products obtained by different producers. The condition is, however, that the products are received through the same or similar chemical processes. The other important factor is application of a well defined measuring background.

4. All the applied spectroscopic methods are quick, cheap and non-destructive. All the analyses can help the producers to compare their products and quality testing.

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