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VEGETABLE OILS AS ADDITIVES TO IMPROVE THE LUBRICITY OF LOW-SULPHUR FUELS

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Abstract

The aim of the study was to determine the sulphur content in 33 samples of oils pressed from different species of vegetable. The unconventional oil samples were purchased from commercial store. Oils was analysed in terms of sulphur content according to the method using X-ray fluorescence spectrometry with wave dispersion, that is described in the PN-EN ISO 20884, 2012 standard. Obtained results of sulphur analysis were presented as the arithmetic mean ± standard deviation (from three replicates) and statistically analysed using the Statistica 13.0 PL program. In order to indicate significance of differences between oils analysis of variance (ANOVA) with Tukey's test of $p \leq 0.05$ significance level was used. The statistical analysis indicated significant differences in the content of sulphur content in the analysed vegetable oils, which could affect the lubricity of prepared fuel blends and in some cases significantly, increase the sulphur content above acceptable value 10 ppm. It was concluded that vegetable oils could be a suitable raw material improving the lubricating properties of low-sulphur diesel oils. However, due to significant differences in the sulphur content in the analysed samples, the content of this element should be analysed beforehand in order to eliminate the possibility of exceeding the permissible level of sulphur in transport fuels.

Keywords: *sulphur content, different species, vegetable oils, biofuel production, lubricity*

1. Introduction

The sulfuric organic compounds found in plants are dominated by amino acids – methionine, cysteine and cystane dipeptide. In addition glutathione, sulfolipids, biotin and glucosinolates can also be found [2, 18]. Generally, sulphur content in plants is in the limit of 0.7 to 14 g/kg of dry matter; however, it usually fluctuates in the range of 2.0-4.0 g/kg. The content of this element depends on the species, i.e. the mass demand for sulphur decreases according to the scheme: cruciferous and crassulae plants > butterfly plants > grasses. Another factor conditioning its content is the richness of the environment with this element (soil richness in soluble sulphates and air pollution). The individual parts of the plant differ significantly in terms of sulphur content, e.g. roots are poorer in this element than the aboveground parts [2]. Zhong et al. (2011) analysing the sulphur content in particular parts of rapeseed sated that, in the roots of this plant sulphur was present in the amount of 1 g/kg, in the stem of about 2.8 g/kg, in pods 8.3 g/kg, while in seeds 4.75 g/kg [27]. In addition, the sulphur content in the dry mass of young plants is higher than of older plants [2].

A deficiency of this element in crop plants may affect the deterioration of crop yield, which, for example in rapeseed plants, is associated with the occurrence of discoloration of flowers, reduction in the amount of siliques, and the amount of rapeseeds. What's more, plants grow much slower and take on a slender appearance. All these factors determine the quality and quantity of raw material [4]. Sulphur also has many important functions in plants. It is essential for the formation of amino acids, proteins, fat and chlorophyll [5]. It also plays a key role in the activation of certain enzymes and vitamins [18]. The level of this compound in the plant also affects the mass of 1000 seeds [24]. From a nutritional point of view, sulphur-containing compounds, i.e. erucic acid and glucosinolates, with a specific bitter taste, are considered to be toxic to humans and animals [21]. The permissible level of these compounds in the case of erucic acid is not more than 2% in oil, while in the case of glucosinolates not more than 30 μmol/g [10, 14]. It is also believed that sulphur oxides are particularly harmful to human health, and in particular colourless sulphur dioxide with an acute stifling and biting odour and a strong irritant of the respiratory tract. This compound penetrates into the body through the nasal mucosa and the upper respiratory tract. The main reason for the formation of SO_2 is the burning of fossil fuels containing significant amounts of this compound, which, as a result of the rehydration with the water contained in the air, generates the formation of acid rain [20]. The adverse effect of this compound on human health and the environment caused that the required sulphur level was reduced to 10 ppm in fuels intended for transport purposes. The main method allowing effective reduction of sulphur content in fuels is hydro ethanol. However, it should be remembered that with the reduction of sulphur content, there has been a significant deterioration of the intrinsic properties of these products, which also translates into their shorter life. Laboratory SR (2007) and Agarwal et al. (2013) stated that lubrication of fuel products is essential to the engine components in order to reduce the friction between the mating components [16, 1]. Commonly, fuels with insufficient lubricity, due to the low lubricating ingredients content, are considered as „dry fuel". However, not only the reduction of the sulphur content causes deterioration of the lubricity of fuels, but also it is mainly affected by removing other available complex fleece during desulphurisation. Available complex polar substances, which created protective layers on the metal surfaces, are as a natural lubricant. Among them oxygen-, nitrogen-, aromatics, and olefinic contents are listed [1, 3, 11].

Vegetable oils that are mainly consist of triacylglycerides and small amounts of non-diacylglycerol compounds such as phospholipids, free fatty acids, sterols, tocopherols, dyes, flavonoids and glycolipids. The triacylglycerol with amphiphilic character, resulted from their structure with long fatty acid chains and presence of polar groups, are considered as good lubricants. Molecules of these compounds orient themselves with the polar end at the solid surface making a closed packed monomolecular or multimolecular layer, contributing to a surface film that provides a desirable lubricity [23]. However, Fox and Stachowiak (2007) stated that vegetable oil in their natural form might not be suitable as lubricants, because of their poor oxidative stability and low temperature properties [8]. What is more, cited authors suggested that these products could be used effectively as additives, in order to improve the polarity behaviour of non-polar base fluid solutions, what would improve tribological performance. Van Gerpen et al. (1998), examining the lubricity properties of soybean oil and soybean methyl esters when used as lubricity additives, observed that biodiesel was slightly more effective than soybean oil [26]. Furthermore, Lang et al. (2001) and Hughes et al. (2002) stated that lubricity properties of biodiesel depended on the fatty acid compositions and kind of alcohol that was used during transesterification process [17, 13]. What is more, Geller Goodrum (2004) and Matzke et al. (2009) found that the individual fatty acid esters did not have as dramatic an effect on lubricity as did methyl esters derived from vegetable oils composed of a mixture of several fatty acids [9,19]. What is more, Kenesey and Ecker (2003) stated that ethyl esters, in comparison to methyl ones of the same oil, were characterized by better lubricity properties [15]. Cited authors also claimed that improved lubricity properties were noticed for unsaturated fatty acids, in comparison to the saturated fatty acids. Fernando et al. (2007) pointed that the main compounds that determined the lubricity of biodiesels were methyl esters and monoglycerides [7]. The effect of free fatty acids, diglycerides and triglycerides on the biodiesel lubricity was not as strong as monoglycerides.

However, those current scientific studies present results that clearly indicate the advantage of vegetable oils used as fuel for diesel engines than biodiesel – that is, methyl esters of higher fatty acids obtained as a result of transesterification of vegetable oils [6, 12]. Estaban et al. (2011), analysing the entire life cycle of vegetable oils and biodiesel, found that oils, in comparison to biodiesel, produced a lower amount of emission during entire life cycle [6]. Similar conclusion has been presented by Hossain and Davies (2010) [12]. What is more, in case of oil samples ratio of produced and consumed energy was better. Oils are renewable, biodegradable and are characterized by low environmental impact and its usage as a fuel in tropical, developing countries would be without obstacles [20,22,25], while in others regions, characterized by lower daily temperatures, the technical innovations of engines (e.g. electric preheating) should be used and/or blending with diesel or dual-fuelling should be conducted.

Considering the above, the aim of the work was to determine the sulphur content in various vegetable oils widely available on the market, to check whether their addition would affect the increased sulphur content, whose maximum content in transport fuels should not exceed 10 ppm.

2. Material and method

The research material consisted of 33 samples of pressed, vegetable oils. Among them oils from seeds, kernels, sprouts of amaranth, watermelon, argan, chokeberry, avocado, baobab, cotton, blackcurrant, black cumin I, black cumin II, red raspberries, wild rose I, wild rose II, inca inchi, rowanberry I, rowanberry II, blackberry, green coffee, wheat germ, macadamia, combo butter, apricot I, apricot II, borage, sea buckthorn I, sea buckthorn II, rose musk, plum, tamanu, strawberries, cherry, cranberry and rapeseed were analysed.

Each of the purchased oils was analysed in terms of sulphur content according to the method using X-ray fluorescence spectrometry with wave dispersion. For the determination, the method described in the PN-EN ISO 20884, 2012 standard was adopted and sulphur analyser Sindie ISO was used.

Obtained results of sulphur analysis were presented as the arithmetic mean ± standard deviation (from three replicates) and statistically analysed using the Statistica 13.0 PL (StatSoft, Cracow, Poland) program. In order to indicate significance of differences between oils analysis of variance (ANOVA) with Tukey's test of $p \leq 0.05$ significance level was used.

3. Results

The statistical analysis carried out on the results of sulphur analysis indicated significant differences in the content of this compound in the analysed vegetable oils. It was shown that rapeseed oil was characterized by the lowest sulphur content (2.12 ppm), while the highest content of this compound was found in the sample of wheat germ (10.09 ppm) (Tab. 1). Among 33 analysed samples, 13 of them (samples of argan, avocado, baobab, borage, green coffee, plum, rapeseed, red raspberries, rowanberry II, sea buskthorn II, watermelon, wild rose I) were characterized by lower sulphur content not exceeding 3.00 ppm. In turn, in the next 9 of them (samples of black cumin II, blackberry, blackcurrant, cherry, chokeberry, rowanberry I, sea buckthorn I, strawberries, wild rose II) the content of this compound was below 4.00 ppm, in 4 next (samples of cotton, cranberry, macadamia, rose musk) sulphur content did not exceed 5.00 ppm, and the content this compound in the apricot II, black cumin I and tamanu samples were close to 6.00 ppm. Higher sulphur content (from 7.36 to 10.09 ppm) was found in the last 4 samples (amaranth, apricot I, combo butter, wheat germ).

The addition of oils with an increased sulphur content may affect the overall content of this element in the prepared fuel mixtures. Therefore, oils for fuel purposes should have been previously tested in order to sulphur content.

Tab. 1. Sulphur content in analysed oils

No.	Oil pressed from seeds/kernels/sprouts	Sulphur content
1	amaranth	7.36$^{\text{b}}$ ± 0.24
2	apricot I	7.85$^{\text{b}}$ ± 0.26
3	apricot II	5.42$^{\text{cde}}$ ± 0.25
4	argan	2.58 $^{\text{klł}}$ ± 0.17
5	avocado	2.65$^{\text{klł}}$ ± 0.23
6	baobab	2.63$^{\text{klł}}$ ± 0.21
7	black cumin I	5.64$^{\text{cd}}$ ± 0.20
8	black cumin II	3.27$^{\text{hijkl}}$ ± 0.18
9	blackberry	3.17$^{\text{hijklł}}$ ± 0.09
10	blackcurrant	3.40$^{\text{hijk}}$ ± 0.21
11	borage	2.92$^{\text{ijklł}}$ ± 0.09
12	cherry	3.88$^{\text{gh}}$ ± 0.29
13	chokeberry	3.06$^{\text{ijklł}}$ ± 0.11
14	combo butter	9.53$^{\text{a}}$ ± 0.23
15	cotton	4.79$^{\text{ef}}$ ± 0.08
16	cranberry	4.85$^{\text{def}}$ ± 0.10
17	green coffee	2.52$^{\text{lł}}$ ± 0.24
18	inca inchi	2.84$^{\text{ijklł}}$ ± 0.16
19	macadamia	4.88$^{\text{def}}$ ± 0.23
20	plum	2.63$^{\text{klł}}$ ± 0.06
21	rapeseed	2.12$^{\text{m}}$ ± 0.10
22	red raspberries	2.68$^{\text{klł}}$ ± 0.12
23	rose musk	4.23$^{\text{fg}}$ ± 0.18
24	rowanberry I	3.51$^{\text{ghij}}$ ± 0.24
25	rowanberry II	2.69$^{\text{klł}}$ ± 0.13
26	sea buckthorn I	3.18$^{\text{hijklł}}$ ± 0.19
27	sea buckthorn II	2.92$^{\text{ijklł}}$ ± 0.13
28	strawberries	3.06$^{\text{ijklł}}$ ± 0.05
29	tamanu	5.96$^{\text{c}}$ ± 0.04
30	watermelon	2.36$^{\text{ł}}$ ± 0.25
31	wheat germ	10.09$^{\text{a}}$ ± 0.16
32	wild rose I	2.71$^{\text{jklł}}$ ± 0.15
33	wild rose II	3.56$^{\text{ghi}}$ ± 0.17

** a, b... – mean values in column marked with the same letter are not significantly different ($p \leq 0.05$)*

4. Conclusion

On the basis of the conducted research, it was concluded that vegetable oils could be a suitable raw material improving the lubricating properties of low-sulphur diesel oils. However, due to significant differences in the sulphur content in the analysed samples, the content of this element should be analysed beforehand in order to eliminate the possibility of exceeding the permissible level of sulphur in transport fuels.

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