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THE EFFECT OF THE ULTRASOUNDS TREATMENT ON FRYING OILS INTENDED FOR BIODIESEL PRODUCTION

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Abstract

The aim of the study was to determine the ultrasounds treatment of frying oil on their properties important in order to biodiesel production. The research material was a frying oil, which prior to transesterification oil was treated with ultrasounds (37 kHz) during 15, 30 and 60 min. In next step, prepared samples were analysed in terms of fatty acid composition, acid value, FFA % and then subjected to alkali transesterification process. After producing methyl esters the yield of biodiesel was analysed with thin liquid chromatography technique (TLC), and then samples were characterized in terms of viscosity in 40 °C, density at 15 °C, acid value, sulphur content and flash point. The results showed that an ultrasonic treatment had a little impact on the fatty acid composition of the test samples. The yield of biodiesel was the higher the longer time of ultrasounds treatment were used. One the other hand, determined with thin liquid chromatography technique yield of biodiesel was the higher the longer time of ultrasounds treatment were used. What is more, the ultrasounds treatment of oil before transesterification process had no impact on viscosity, density and acid value of these samples, while flash point values and sulphur content were changed.

Keywords: *frying oil, ultrasounds, fatty acids composition, transesterification, yield of biodiesel*

1. Introduction

A common method of biodiesel production is a transesterification in which vegetable oils (rapeseed, sunflower, soybean, corn, palm oil), alcohol (methanol or ethanol), and the alkali catalyst (NaOH, KOH) are mainly used. During the reaction of rapeseed oil (triglycerides) with methanol and potassium hydroxide are formed two phases, which differ in both physical and chemical properties. The upper phase – the fuel – is a fatty acid methyl esters, while the lower phase – glycerol phase. In each of these product phases may occur the minor components as a result of incomplete transesterification process, such as mono- and diacylglycerols, products of acids hydrolysis, fatty acid salts (soap), phospholipids and others [11]. The factors determining the efficiency of the transesterification process include type of alcohol; the molar ratio of alcohol to the oil; type and concentration of the catalyst, temperature and time of reaction and mixing. In the case of the selection of the alcohol, its price and performance are taken into consideration [5]. In most scientific papers methanol are commonly used due to its low cost, easy availability and recovery after the transesterification process [1, 5, 6, 9, 13, 15, 21, 23].

According to research conducted by Colucci et al. ultrasound treatment of reaction mixture during mixing oil with alcohol can improve yield of biodiesel production [4]. Cited authors explain that during typical transesterification process production of emulsion from oil, alcohol is hampered due to the different nature of these two phases, and therefore vigorous stirring is necessary. Colucci et al. suggested that, in order to facilitate the emulsification process ultrasounds treatment should be used [4]. As Hanh et al. explained ultrasonic nozzles induce hitting one of liquid particle to another one and cause the disintegration of cavitation bubbles, which in turn distorts the phase boundary and results in emulsification [7]. Cited authors generally found that the application of ultrasound during stirring of the reaction mixture improves the rate of mass transfer of triglycerides from the oil to methanol, provides faster reaction times, lower cost of reagents and less drastic parameters of process, which in turn generates a lower cost of production. On the other hand, it would fall well as see how the same ultrasound affect the fatty acid profile for the production of biodiesel and biofuel characteristics produced based on this oil. That is to be taken in this paper.

On the other hand, it should be also checked whether the ultrasound treatment of oil before transesterification process would affect its chemical and on the characteristics of biofuels produced based on this oil. That problem was taken in to consideration in the present study.

2. Material and methods

The research material was a frying oil obtained from a restaurant located in Olsztyn, in Poland. After receiving, the frying oil has been subjected to pre-treatment, i.e. the removal of solids (particles of fried food). Then the sample was subjected to chemical analysis to determine the acid number, which value determines the choice of the appropriate method of transesterification. However, prior to transesterification oil was treated with ultrasounds (37 kHz) in an ultrasonic bath (Elma D-78244 Singen S60Hl, Germany) during 15, 30 and 60 minutes, and then tested for fatty acid composition according to (PN EN ISO 12966-1, 2015). In next step, after estimating the acid value (2.53 mg KOH/g oil) %FFA (free fatty acids) was calculated (%FFA=1.27%). Zhang et al. [22] and Özbay et al. [10] reported that during the base transesterification process, oil with a greater than 0.05% share of FFA can be saponified, which reduces the yield of the transesterification process. By contrast, during acid transesterification FFA occurring at too high amount react with alcohol and produce esters and water, which inhibits the transesterification [3].

According to Tańska et al., oils with a higher share of FFA should first be subjected to a de-acidification process or subjected to transesterification with acid catalyst [17]. On the other hand, Wang et al. pointed out that oils characterized by higher share of FFA than 10% should be transesterified with acid catalyst using the apparatus of stainless steel, with a much higher addition of methanol and at higher pressure conditions (170-180 kPa) [20]. Data presented above and established value of the acid value and FFA %, allowed stating that appropriate method of biodiesel production would be alkaline transesterification carried out in accordance with the method described by Ambrosewicz-Walacik et al. [2].

After transesterification process the yield of biodiesel was analysed with thin liquid chromatography technique (TLC), and then samples were characterized in term of: viscosity in 40°C (PN-EN 3104, 2004), density at 15 °C (PN-EN ISO 3675, 2004), acid value (PN-EN 14104, 2004), sulphur content (PN-EN ISO 20884, 2012), flash point ((PN-EN ISO 2719, 2007).

3. Results and discussion

One of the most important quality factor of oils intended to biodiesel production is share of unsaturated fatty acids. Amount of these compounds in oils affects their viscosity and freezing point – with increasing amounts of them the lower value of these discriminants. One the other hand, these oils are characterized by low oxidative stability and have a greater ability to polymerization, which contributes to the formation of carbon deposits the elements of the injection system and combustion chambers of the engine [2, 16, 19]. Pilarski found that using of oils with high saturated fatty acids as a fuels to power compression ignition engines of tractors is not possible because of the fact that these oils solidify at room temperature [14]. The results showed that an ultrasonic treatment had a little impact on the fatty acid composition of the test samples (Tab. 1). In case of 15 min ultrasounds treatment the small decrease of linolenic acid, linoleic acids share was observed, while share of oleic and palmitic acid increased. Sample of oil that was treated with ultrasounds by 30 min was characterized by a similar saturated, monounsaturated and polyunsaturated fatty acids composition in comparison to the reference sample. On the other hand, among all samples oil treated for the longest time with ultrasound was characterized the highest increase of oleic acid (1.3 percentage points) and decrease of palmitic acid.

Tab. 1. Fatty acids composition of reference sample and oils treated with ultrasounds

Fatty acids	Time of ultrasounds treatment			
	without	15 min	30 min	60 min
$C_{14:0}$ myristic acid	0.15±0.00	0.16±0.01	0.17±0.02	0.15±0.01
$C_{16:0}$ palmitic acid	7.57±0.01	7.84±0.04	7.68±0.03	7.38±0.42
$C_{16:1}$ palmitoleic acid	0.21±0.01	0.20±0.01	0.21±0.01	0.20±0.02
$C_{18:0}$ stearic acid	3.26±0.04	3.19±0.37	3.44±0.41	2.94±0.17
$C_{18:1}$ oleic acid	76.68±0.06	77.38±0.93	76.02±1.18	77.98±0.95
$C_{18:2}$ linoleic acid	7.78±0.04	6.88±0.38	8.04±0.13	7.18±0.15
$C_{18:3}$ linolenic	0.48±0.02	0.42±0.08	0.51±0.04	0.47±0.06
$C_{20:0}$ arachidic	0.88±0.03	0.97±0.06	0.98±0.21	0.83±0.04
$C_{20:1}$ eicosenoic	1.88±0.01	1.72±0.12	1.86±0.29	1.68±0.01
$C_{22:0}$ behenic	0.27±0.00	0.43±0.28	0.19±0.10	0.40±0.06
others	0.86±0.02	0.84±0.13	0.92±0.13	0.82±0.05
saturated	**11.25**	**11.61**	**11.48**	**10.87**
monounsaturated	**78.77**	**79.30**	**78.08**	**79.85**
polyunsaturated	**9.13**	**8.26**	**9.52**	**8.47**

Determined with thin liquid chromatography technique yield of biodiesel has been the higher the longer time of ultrasounds treatment were used (Fig. 1).

The yield of biodiesel obtained from reference sample was lower that samples produced from oil treated with the shortest time of ultrasounds. The highest conversion of triacylglycerols was observed in sample produced from oil treated 60 min with ultrasounds (2.43 percentage points in comparison to reference sample), and then of biodiesel obtained from oil treated with 30 min of that factor. Teixeira et al. analysing transesterification of fatty acids by means of ultrasonic energy also observed an increase in yield of biodiesel obtained from beef tallow (approx. 1 percentage points) [18]. Similar results were obtain by Ji et al. [8]. Cited authors investigated an alkali-catalysed biodiesel production method with power ultrasonic (19.7 kHz) and they found a similar tendency to that found in the presented work. During transesterification carry out with 5 min ultrasounds treatment, approx. 85% yield of biodiesel was obtained. In case of longer treatment (10 and 20 min) level of conversion reached almost 100%.

Fig. 1. TLC chromatograms of esters obtained by single-base esterification from different oils: a) reference sample, b) 15 min ultrasounds treatment, c) 30 min ultrasounds treatment, d) 60 min ultrasounds treatment

It was found that an ultrasounds treatment had no impact on viscosity, density and acid value of these samples. On the other hand, changes in flash point values and sulphur content was observed. In case of a flash point, it was found that in comparison to biodiesel produced from reference sample, all samples treated with ultrasounds were characterized by lower value of that parameter. However, with longer duration ultrasounds treatment a flash point of analysed fuels increased. An adverse tendency was observed in case of sulphur content. Biodiesel produced from oils exposed to long periods of ultrasounds treatment were characterized by lower content of this element.

Tab. 2. Physicochemical characteristics of biofuels

Discriminants	Time of ultrasounds treatment on oils intended for biodiesel production			
	0 min	15 min	30 min	60 min
yield of biodiesel [%]	85.23	86.71	87.40	87.66
viscosity in 40 °C [mm^2/s]	3.65	3.69	3.68	3.63
density in 15 °C [kg/m^3]	877	876	878	876
flash point [°C]	190	145	155	170
acid value [mg KOH/g]	0.06	0.05	0.06	0.06
sulphur content [mg/kg]	2.60	1.98	1.93	1.33

4. Conclusions

1. The ultrasounds treatment had a little impact of fatty acids composition of analysed frying oil.
2. The yield of biodiesel was the higher the longer time of ultrasounds treatment were used.
3. The ultrasounds treatment of oil before transesterification process had no impact on viscosity, density and acid value of these samples, while flash point values and sulphur content were changed.

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