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Influence of tested parameters on biodiesel quality obtained from used and unused vegetable oil

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Abstract: The aim of this study was to obtain biodiesel, synthesized by transesterification from used (waste) and unused (industrial) sunflower vegetable oil, purify with following solvents: distilled water, 4% H_3PO_4 and 4% HCl, determine biodiesel quality parameters, and finally analyze the influence of the selected parameters and used solvents for purification on the content of soap in biodiesel. Rinsing of biodiesel for each used solvent was carried out 2, 3, 5, 7 and 9 times with a certain amount of above-mentioned solvents. Differences in the values of selected parameters (indicators) of biodiesel quality as well as the concentration of soap in the purified biodiesel between single rinses for the used solvents were observed, and the values of the examined parameters between different purifiers with the same rinse number were compared. In this study, the estimated effects of washing methods on biodiesel density, kinematic viscosity, acid number, peroxide number, flash point, and biodiesel synthesis yield were determined. It was found that there were no significant changes and deviations of the obtained values of the examined parameters, when purifying biodiesel with different solvents (for both type of used oils), except for the value of the peroxide number for acid washing. Based on the results obtained in this work, acid solution is better for soap removal.

INTRODUCTION

Recently, biodegradable biofuels replace traditional fossil fuels, and most researchers talk about biofuels as a perfect renewable source of energy. Its main advantages are biodegradability, non-toxicity by its nature, low emission profile, which reduces global warming and is therefore environmentally friendly (Krawczyk, 1996; Mittelbach and Tritthart, 1988; Srivastava and Prasad, 2000; Dorado *et al.*, 2003; Tashtoush, Al-Widyan and Al-Shyoukh, 2003; Labeckas and Slavinskas, 2006). It is chemically defined as fatty acid methyl ester. Its production is of significance because it represents an environmentally acceptable alternative fuel for diesel engines. Biodiesel can be produced from a variety of raw materials such as edible vegetable oils, inedible vegetable oils, animal fats, recycled fats and oils, waste edible oils, waste materials (fat from oil and fat separators), by-products from edible oil production processes etc. (Demirbas, 2003; Frohlich and Rice, 2005; Bhati *et al.*, 2008; Issariyakul *et al*., 2008; Singh and Singh, 2009; Schinas *et al*., 2009; Hameed *et al*., 2009). Secondary raw materials, i.e. those that remain as waste from other industries and households, which were also used in this paper, were found very useful. Most of today's mass-production of biodiesel is based on the chemical transesterification reaction of triglyceride with an alcohol (usually methanol) using a base catalyst (Ferella *et al*., 2010; Leung *et al*., 2010). The transesterification process itself depends on the parameters such as temperature, pressure, reaction time, mixing rate, type and molar ratio of the used alcohol, type and concentration of the used catalyst, moisture concentration, the amount of free fatty acids used for the synthesis of biodiesel. The optimum values of the above parameters to achieve maximum conversion depend largely on the physical and chemical properties

of the raw material (Banerjee and Chakraborty, 2009). Once produced mixture of fatty acid methyl ester (crude biodiesel) should be subjected to the purification process to meet the specifications specified by appropriate standards such as EN 14214 or ASTM D6751. The performance of biodiesel as an alternative fuel for diesel engines depends on its purity (Banga and Varshney, 2010). Impurities reduce biodiesel quality and affect engine performance through a number of negative effects (Atadashi *et al*., 2011; Berrios and Skelton, 2008). The purification of crude biodiesel is usually achieved via two notable techniques; wet and dry washings. This process is necessary to remove various types of contaminants such as unconverted triacylglycerols, diacylglycerols, free fatty acids, glycerol, water, catalyst, soaps, etc. from crude biodiesel, thus preventing any significant eventually diesel engine damage. The quality of biodiesel fuel is determined by a set of indicators, such as the kinematic viscosity, density, oxidation stability, lubricity, quality of fuel ignition expressed in cetane number, etc (Tai Shung, 2007, Sharma & Singh, 2008, Demirbas, 2009).
The aim of this study was to obtained biodiesel, synthesized by transesterification from used and unused sunflower vegetable oil, purify with solvents: distilled water, 4% H_3PO_4 and HCl, determine the quality parameters of biodiesel and finally analyze the influence of the selected parameters and the used solvents for purification on the content of soap in biodiesel.

EXPERIMENTAL

All chemicals used in this study were of thehigh purity grade.

Sample preparation: For synthesis of biodiesel two types of vegetable oil were used: pure "BIMAL FINO" oil, which is a mixture of sunflower, rapeseed and soybean oil, produced by BIMAL d.d. Brčko and used, waste oil from the working restaurant. The waste oil collected during one week from the restaurant was mainly used for frying meat and vegetables. It was first decanted to remove the largestfood residues and then purified by vacuum filtration in order to eliminate the presence of mechanical contamination (food residues). After filtration, both types of oil were heated up to 110-120°C to remove any water present.

Synthesis and purification of biodisel: Conventional synthesis of biodiesel was carried out at 60-65°C with constant mixing (magnetic stirrer) during 120-150 min. Cooling and separation of glycerol from biodiesel was carried out during 4h. Methanol:oil molar ratio was 6:1 (Banerjee and Chakraborty, 2009; Stojkovic *et al*., 2014). A total of 6 synthesis were carried out, 3 for used and 3 for unused (pure) sunflower oil. Purification of the obtained biodiesel was done by a wet process and consisted of 2, 3, 5, 7 and 9 washings using distilled water, 4% H_3PO_4 and 4% HCl.

Characterization: Product characterization, after purification, was done after each wash (2, 3, 5, 7, 9 rinsing) by viscosity measurement (Ostwald), density measurement (pycnometer), flash point measurement (Marcuson), yield calculation (Vatrenjak-Velagić, 1997). The same quality parameters were determined for used and unused oil before the production of biodiesel. The content of soap in obtained biodiesel was determined by the titrimetric method.

RESULTS AND DISCUSSION

The characterization of used (waste) and unused (pure) oils was carried out prior to the synthesis of biodiesel. The requirements for edible oils indicate that the value of their acid number should not be higher than 0.6 mg KOH/g, and the peroxide number may be up to 5.0 mmol/kg. Based on the obtained results (Table 1) it can be concluded that the density, viscosity and acid number for pure and used oil are very similar, i.e. there are no significant differences, but it cannot be observed for the peroxide number. Compared to value of peroxide number obtained for pure oil (2.30) and the used oil (3.927), a greater difference can be observed with respect to other parameters. And compared to reference values the difference is even greater. Autooxidation is considered as the main cause of difference between the references values and obtained values of peroxide number, since the waste oil used in this study was exposed to high temperatures, oxygen from the air, and it also contained a water from the food. Andričić, Kovačić and Čagalj (2008) have also used the waste and pure edible sunflower oil, and obtained the following values for density, acid number and peroxide number for pure oil: 0.915 g/mL, 0.163 mgKOH/g and 9.8 mmol/kg. While for the waste oil (in the same order) values were: 0.915 g/mL, 0.416 mg KOH/g and 21.2 mmol/kg.

Table 1. Quality parameters of oils used for the synthesis of biodiesel.

Parameter	Acid number (mgKOH/g)	Peroxide number (mmol/kg)	Density (g/cm^{-3})	Viscosity (E°) at 20°C
Pure oil	0.112	2.30	0.919	8.76
Used (waste) oil	0.149	3.927	0.922	8.66
Reference for pure oil	0.163	9.80	0.915	/
Reference for used (waste) oil	0.416	21.2	0.915	/

Synthesis of biodiesel

A total of 6 syntheses was carried out, of which for 3 was used pure vegetable oil, and for 3 was used oil from the restaurant, previously processed. In Table 2 and 3 are given the amounts of the substances for synthesis and obtained yields for rinsing with distilled water. Based on the obtained yields (Table 2 and 3) for synthesized biodiesel, it can be concluded that these are high values in comparison to Andričić, Kovačić and Čagalj (2008). In this study (Andričić, Kovačić and Čagalj 2008) transesterification was carried out in a reactor with a stirrer at 60°C with methanol and KOH as a catalyst.

Obtained yield for biodiesel produced from pure oil was 83% and the yield for biodiesel produced from used oil was 81%. The yield was calculated as in this paper, i.e. relative to triglyceride olein, since the oleic acid esters are most commonly present in edible oils.

Table 2. Amounts of substances used for the synthesis of biodiesel from pure oil and the resulting yields for washing with distilled water.

Synthesis	Mass of oil (g)	Mass of KOH (g)	Volume of methanol (mL)	Mass of biodiesel (g)	Yield (%)
1.	500.29	5.01	137.30	467.79	93.50
2.	500.26	5.08	137.38	461.34	92.22
3.	500.48	5.04	137.44	455.34	90.48

Table 3. Amounts of substances used for the synthesis of biodiesel from waste oil and resulting yields for washing with distilled water.

Synthesis	Mass of oil (g)	Mass of KOH (g)	Volume of methanol (mL)	Mass of biodiesel (g)	Yield (%)
1.	500.09	5.00	137.33	477.86	95.55
2.	500.16	5.02	137.35	466.77	93.32
3.	500.15	4.99	137.35	467.57	93.48

Purification of synthesized biodiesel and determination of quality parameters

Distilled water, 4% H_3PO_4 and 5% HCl were used as the solvents for the purification of the synthesized biodiesel:. For all three solvents, the rinsing process was the same as the rinsing time, as well as the amount of used rinsing solvent. Characterization of biodiesel after rinsing with any of the three mentioned solvents was carried out after 2, 3, 5, 7 and 9 rinsing.

Determination of biodiesel density after purification

Density values of biodiesels, purified by water washing, were between 0.8783-0.8826 g/cm^3 (biodiesel obtained from pure oil), and 0.8793-0.8845 g/cm^3 (biodiesel obtained from used oil), complying the EN 14214 standard limits. For biodiesel purified by acid washing, obtained density values were between 0.8787-0.8817 g/cm^3 (biodiesel obtained from pure oil), and between 0.8796-0.8830 g/cm^3 (biodiesel obtained from used oil), complying the EN 14214 standard limits. According to EN 14214, biodiesel density values should be within the recommended limits of 0.860 to 0.890 g/mL. Obtained results from this study (Figure1) are also confirmed by the literature data (Ljupković, 2014) where the value of density was 0.8884 g/mL, while the value of biodiesel density in the work (Lučić, 2015) was 0.8868 g/mL. Gligorijević *et al.* (2010) conducted experiments with aim to compare the density of diesel and biodiesel fuel, density of diesel fuel was 0.84 g/mL, and density of biodiesel was 0.88 g/mL, so it is noticeable, biodiesel fuel has a higher density than diesel fuel.

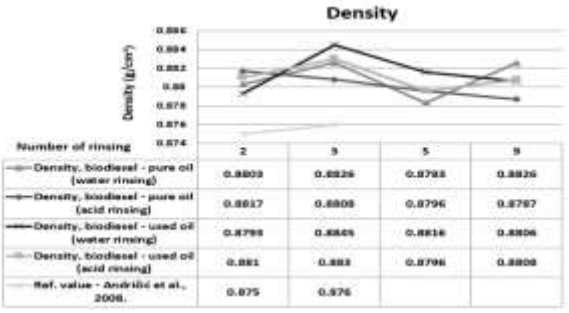

Figure 1. *Dependence of biodiesel density from the solvents for purification*

Determination of biodiesel viscosity after purification

According to EN 14214, the values of biodiesel viscosity should be within the recommended limits of 1.263-1.394°E, while according to American Standard ASTM D6751, the recommended viscosity values for biodiesel are 1.1195-1.482°E. Based on the obtained results for viscosity of biodiesel, all obtained values are within the recommended limits (for biodiesel obtained from pure and used oil). The results from this paper are also confirmed by the literature data (Ljupković, 2014) where the value of biodiesel viscosity was 1.342°E, while the value of biodiesel viscosity in the work (Kovač, Saravan and Šikuljak, 2012) was 1.359°E.

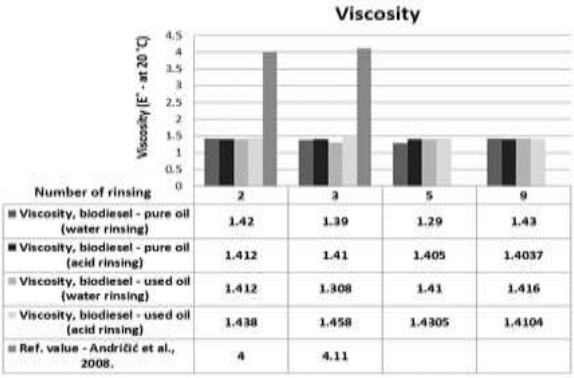

Figure 2. *Dependence of biodiesel viscosity from the solvents for purification*

Determination of acid number of biodiesel after purification

Acid numbers of biodiesels purified by water washing were between 0.0547-0.0652 mgKOH/g (biodiesel obtained from pure oil), and 0.0652-0.0745 mgKOH/g (biodiesel obtained from used oil). Acid numbers of biodiesels purified by acid washing were 0.0418-0.0559 mgKOH/g (biodiesel obtained from pure oil), and 0.0604-0.0671 mgKOH/g (biodiesel obtained from used oil). According to EN 14214, value of the acid number of biodiesel shouldn´t exceed the recommended upper limit of 0.50 mgKOH/g, while according to American standard ASTM D6571-02, recommended acid number is 0.80 mgKOH/g. The results from this work are also confirmed by the literature data (Andričić, Kovačić and Čagalj, 2008) and (Ljupković, 2014).

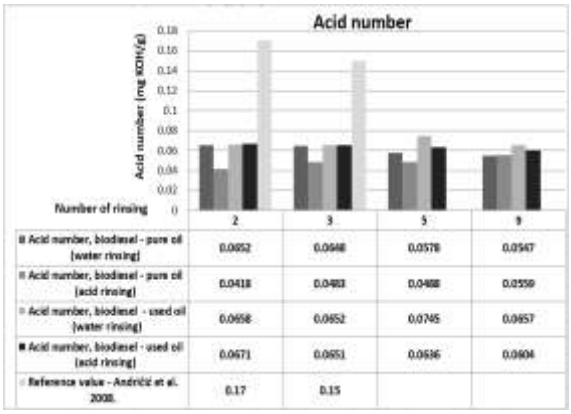

Figure 3. *Dependence of biodiesel acid number from the solvents for purification*

Determination of peroxide number of biodiesel after purification

According to EN ISO 3960, the value of the peroxide number of biodiesel should not exceed the recommended upper limit of 10 mmol/kg. From Figure 4, it can be seen that, using acid washing to purify crude biodiesel results in decrease of the value of the peroxide number.

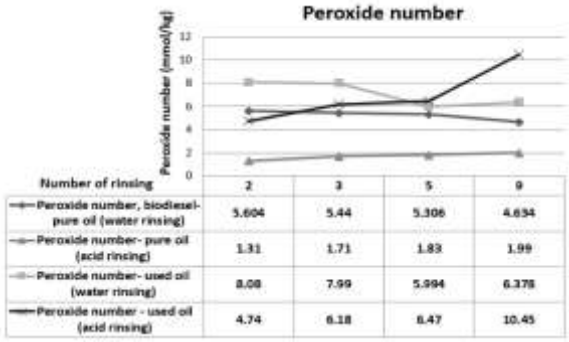

Figure 4. *Dependence of biodiesel peroxide number from the solvents for purification*

Determination of flash point of biodiesel after purification

Flash points for most of synthesized and purified biodiesels are between 170-190°C, what is a satisfactory quality of biodiesel, regardless of the used purification agent. Flash point is generally reduced with an increase in the number of rinsing. According to EN 14214, flash points of biodiesels should notexceed the recommended limit below 120°C. From the obtained values in this study (Figure 5), it was found that all values obtained for the flash point of produced biodiesels are within the recommended limits. Obtained results are also confirmed by the literature data (Andričić, Kovačić and Čagalj, 2008) where the value of the flash points of biodiesels was 182-191°C.

Determination of the soap concentration

Soap concentration for both, unused (pure) and used (waste) oil, decreases with an increase in the number of washings (Figure 6). Considering the results, efficiency of removing impurities in the form of soaps was better when washing was carried out with an acid than with water, regardless of the kind of used raw materials.

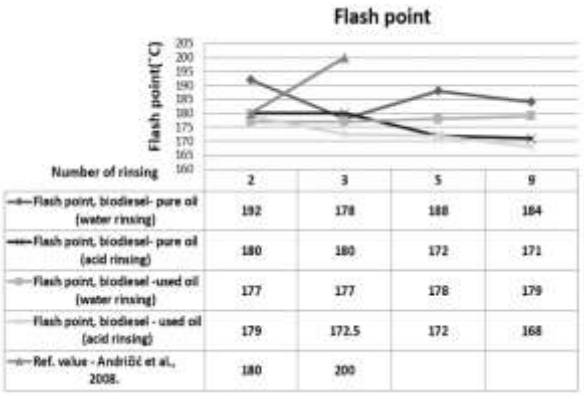

Figure 5. *Dependence of biodiesel flash point number from the solvents for purification*

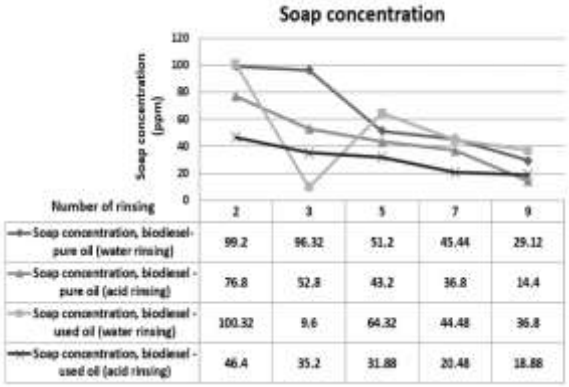

Figure 6. *Dependence of soap concentration from the solvents for purification*

In the study of Predojević et.al (2008) two solvents for purification of biodiesel were compared: hot distilled water and 5% phosphoric acid solution. Influence of wash methods on the biodiesel quality parameters as in this paper (kinematic viscosity, acid value, yield loss etc.) were measured and evaluated. There were no major changes between the two used solvents and investigated parameters. It was established that the phosphoric acid wash decreases the acid value of obtained biodiesel, and produced a higher yield compared to distilled water wash.

CONCLUSIONS

The work has shown that the used solvents for purification of crude biodiesel do not greatly effect on the examined biodiesel quality parameters such as acid number, peroxide number, density, viscosity, and flash point. Washing with all three solvents have proven to be efficient purification techniques. The best results of biodiesel wet washing were with 4% chloride acid, which did not deviate much from the results obtained by distilled water. Analysis of synthesized biodiesels have shown that their quality parameters correspond to the requirements set by the European biodiesel standard. It was also found that the acid solution is better for removing of the soaps, *i.e.* fewer soap concentrations in biodiesel were observed with an increase in the rinsing rate with a 4% H_3PO_4 solution.

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Summary/Sažetak

Cilj ovog rada je dobivanje biodizela, sintetiziran transesterifikacijom iz korištenog (otpadnog) i nekorištenog (industrijskog) suncokretovog biljnog ulja, prečišćen odabranim otapalima (destilovana voda, 4%-tna H_3PO_4 i 4%-tna HCl), određivanje parametara kvalitete biodizela, te u konačnici analiziranje uticaja odabranih parametara i korištenih otapala za prečišćavanje na sadržaj sapuna u biodizelu. Ispiranje biodizela, za svako korišteno otapalo, vršeno je 2, 3, 5, 7 i 9 puta sa određenom količinom navedenih otapala. Praćena je razlika u vrijednostima odabranih parametara (pokazatelja) kvaliteta biodizela, kao i koncentracije sapuna u prečišćenom biodizelu između pojedinačnih ispiranja za korištena otapala, i upoređene su vrijednosti ispitivanih parametara između različitih otapala za prečišćavanje sa istim brojem ispiranja. U ovom istraživanju su procijenjeni učinci metode pranja na gustoću biodizela, kinematičku viskoznost, kiselinski broj, peroksidni broj, tačku paljenja i prinos sinteze biodizela. Utvrđeno je da nema nekih značajnih promjena i odstupanja dobijenih vrijednosti ispitivanih parametara, prilikom prečišćavana biodizela različitim otapalima, kao i prilikom upotrebe otpadnog i čistog biljnog ulja za sintezu biodizela, osim za vrijednost peroksidnog broja pri ispiranju sa kiselinom za korišteno i čisto ulje, te je utvrđeno da otopina kiseline bolje za sobom povlači sapune, tj. zabilježene su manje koncentracije sapuna u biodizelu sa povećanjem broja ispiranja sa 4%-tnom otopinom H_3PO_4.