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FULL PAPER

The Effectiveness of Natural and Synthetic Antioxidant Additives on the Oxidation Stability of Biodiesel Synthesized from Fresh and Waste Sunflower Oil

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Abstract:

Biodiesel fuel is the realistic fuel for the future due to its environmental, economic and energetic benefits. However, the degradation and instability during biodiesel storage and application present the major disadvantages and hence a modern scientific challenge. The aim of this study was to choose optimal parameters for biodiesel synthesis from fresh and waste sunflower cooking oil and to investigate the possibilities of increasing its resistance towards oxidative degradation. Various physico-chemical characteristics essential for the quality estimation of the resulting biodiesel products were compared before testing the effectiveness of natural and synthetic antioxidants. Butylated hydroxytoluene (BHT), carvacrol and α-tocopherol were added to the biodiesel in different concentrations in order to determine their efficiency during the Schaal oven test. Results proved that both, fresh and waste oil can be valuable sources for the synthesis of biodiesel that meets European and American quality standards. Among the antioxidants, BHT was the most efficient one in both types of biodiesel and its usage would be recommended at the concentration of 1000 ppm. The findings present a cost-effective and environmentally friendly source for biodiesel production with improved properties - considerably enhanced resistance to oxidative degradation, where synthetic antioxidants are given the priority.

Keywords: antioxidants; biodiesel; sunflower; waste oil; quality

1. Introduction

Environmental and economic concerns have initiated the search for viable alternatives for fossil fuels. As petroleum sources are decreasing and food supplies have an existential importance much interest has been driven in resolving these issues. Vegetable oil and animal fat are favourable sources for biodiesel production as they are natural, biodegradable and non-toxic materials [1]. However, secondary raw materials, industry and household waste which are no longer suitable for human consumption are readily employed as potential candidates for biodiesel production, as well. The use of biodiesel will allow a balance to be sought between agriculture, economic development, and the environment [2]. Biodiesel is commonly defined as the mono-alkyl esters of vegetable oils or animal fats. It is produced by transesterifying the oil or fat with an alcohol such as methanol under mild conditions in the presence of a base catalyst. The fatty acid profile of biodiesel corresponds to that of the parent oil or fat it is obtained from. The major components of biodiesel fuels are straight-chain fatty acids, the most common ones containing 16 and 18 carbon atoms. The composition of a fuel has significant influence on its properties [3]. During storage, changes occur in composition as well as physico-chemical properties of biodiesel which include acid value (AV), density, viscosity, peroxide value (PV), induction period (IP) and flash point (FP). Hydroperoxides, aldehydes, ketones, and acids are produced during oxidation process and are responsible for the

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change in fuel properties. One of the major issues associated with the use of biodiesel is to maintain the fuel at specified standards for a longer period. Biodiesel is more prone to oxidization than a mineral diesel, and it starts turning rancid within a week or less, and complete degradation occurs after a period of 4 weeks. While oxidation susceptibility is desirable from environmental perspective, it is one of the major technical drawbacks of biodiesel hindering its commercial use in automobile [5]. The issues related to biodiesel degradation are still a current topic which necessitates chemical modifications or other approaches that will enhance its stability. The aim of this work was to bypass the food versus fuel issue by using waste cooking oil (WCO) as a source for biodiesel synthesis, to evaluate and improve its physico-chemical characteristics by investigating the efficiency of natural and synthetic antioxidants in order to provide a model of environmentally friendly and cost-effective biodiesel production.

2. Results and Discussion

2.1. Characterisation of oil

Sunflower is one of the more prominent oilseed crops for biodiesel production and it can grow in a variety of climatic conditions but is considered to be an inefficient user of nutrients [6]. The average yield is 952 L per hectare and oil content is 25–35% [7]. Prior to biodiesel synthesis, the fresh and WCO oil was characterized by measuring the following parameters: density, viscosity, AV and PV. The density values depend on the fatty acid composition as well as on the biodiesel purity. Density increases with decreasing chain length and increasing number of double bonds, or it can be decreased by the presence of low-density contaminants such as methanol [8]. Formation of polymeric secondary oxidation products increases viscosity and can lead to the formation of gums and sediments that clog filters. The time for a volume of liquid to flow under gravity through the viscometer is measured and converted to a viscosity reading [9]. Acid value is expressed in mg KOH required to neutralize 1 g of fatty acid methyl esters (FAME). The parameter characterizes the degree of fuel ageing during storage, as it increases gradually due to degradation of the biodiesel. High fuel acidity has been discussed in the context of corrosion and the formation of deposits within the engine which is why it is limited in biodiesel specifications [10]. Peroxide value, measured in milliequivalents of peroxide per kg of sample, indicates the content of primary products of oxidation; hydroperoxides. Although PV is not specified in biodiesel fuel standards, this parameter influences the cetane number (CN) which is specified in fuel standards; increasing PV increases CN [11].

Table 1. Characteristics of the sunflower oil used for synthesis.

	Density (g/mL) (at 20 °C)	Viscosity (mm^2/s) (at 40 °C)	AV (mg KOH/g)	PV (mmol/kg)
Fresh oil	0.94	30.96	0.07	2.17
Waste oil I	0.91	30.90	0.07	19.19
Waste oil II	0.92	31.30	0.08	16.01
Waste oil III	0.89	35.28	0.07	16.22

While the density, viscosity and AV are similar, the PV in fresh and WCO is significantly different. The high PV in WCO is caused by auto-oxidation processes, exposure to high temperatures and oxygen from the air. The obtained values for viscosity are high, which is why the oil is unsuitable as fuel for cars.

2.2. Biodiesel synthesis and characterisation

The biodiesel synthesis included steps that lead to product loss such as rinsing, drying and filtering, however the yield for the six synthesized biodiesel products was between 88 – 92 %. The colours of biodiesel synthesized from fresh oil and WCO differed but the characterisation (Table 2) confirmed that the coloration is not related to the biodiesel quality. The density values for all biodiesel products are similar and within the range specified in EN 14214. The same is true for viscosity values, however the viscosity of the biodiesel is significantly reduced compared to the oil from which they have been synthesized. The PV of the biodiesel is reduced compared to the

WCO from which it has been synthesized, as well. In biodiesel, the fatty acids are esterified and hence the auto-oxidation is decreased, which all results in a reduction of PV. According to EN 14214, the FP of biodiesel should not be lower than 120 °C. It is defined as the lowest temperature at which a fuel gives off sufficient vapours, which when mixed with air will ignites momentarily [10]. The FP of the synthesized biodiesel were between 179 and 195 °C, suggesting the absence of methanol or other impurities. Higher FP of a fuel indicates that the fuel is safer for handling and storage. Particularly, biodiesel is a safer fuel for handling and storage as it has high FP [5].

Table 2. Characterization of biodiesel.

Biodiesel products	Density (g/mL)	Viscosity (mm^2/s) (at 40 ^0C)	AV (mg KOH/g)	PV (mmol/kg)	FP (^oC)
Biodiesel I (fresh oil)	0.89	3.97	0.06	6.15	195
Biodiesel II (waste oil)	0.88	4.05	0.06	5.67	184
Biodiesel III (fresh oil)	0.87	3.84	0.05	7.95	184
Biodiesel IV (waste oil)	0.86	3.80	0.07	7.46	179.5
Biodiesel V (fresh oil)	0.85	4.43	0.05	7.45	185
Biodiesel VI (waste oil)	0.87	4.26	0.06	6.36	182.5

2.3. Addition of antioxidants

Biodiesel fuel properties can degrade by one or more of the following mechanisms: (i) oxidation or autoxidation from contact with oxygen present in ambient air; (ii) thermal or thermal-oxidative decomposition from excess heat; (iii) hydrolysis from contact with water or moisture in tanks and fuel lines; or (iv) microbial contamination from migration of dust particles or water droplets containing bacteria or fungi into the fuel [12]. The chemistry of biodiesel degradation will be the same as that of the fatty oils from which they are derived and fuel properties within the various biodiesel depend upon feedstock [13]. The susceptibility of biodiesel to oxidation is due to its content of unsaturated fatty acid chains. Further on, the oxidative stability decreases with increases in chain length of the ester side chain [14].

Antioxidants can be added to delay, control or inhibit autoxidation processes of substrates and decrease the yields of unwanted secondary products. The selection of antioxidants involves compromises between conflicting desirable properties. Some of the highly desirable properties are good solubility, effective in low concentrations, long shelf life, and no toxicity [4]. Available antioxidant can be broadly divided into two categories chain breakers and hydroperoxide decomposers [15]. Phenolic and amine-types of antioxidants derived from natural or synthetic source belong to the chain breaker category. The common synthetic phenolic antioxidants are butylated hydroxyanisole (BHA), BHT, propyl gallate (PG), and tertiary butylhydroquinone (TBHQ) [16-17], and natural antioxidants include a wide variety of compunds such as tocopherols, ascorbic acid, carotins, and flavonoids; green tea extracts, pomegrante hull, etc. [18-19]. It has been shown that synthetic antioxidants are more effective than natural antioxidants in improving oxidation stability. However, poor biodegradability and toxicity of most of these antioxidants expressed great concern [20]. For this study, one synthetic and two natural antioxidants were chosen.

According to European standards the rancimat test is the standard method for the determination of biodiesel oxidation stability. In our work, we employed the oven test considering that other authors [21] showed overlapping results between these two tests.

Portions of the obtained biodiesel were treated with antioxidants. Butylated hydroxytoluene, carvacrol and α-tocopherol were added in various concentrations and combinations. After completing the oven test, results showed that the density, viscosity and AV were similar among the biodiesel sample groups (Table 3) and compared to the biodiesel without antioxidants (blank samples). The analysed parameters were all within intervals required by the European (EN 14214) and American (ASTM D 6751) standards for the quality of biodiesel.

Table 3. Biodiesel characterization upon addition of antioxidants and oven test.

Biodiesel sample groups	Density (g/mL) (20 ^{0}C)	Viscosity (mm^2/s) (40^{0}C)	AV (mg KOH/g)
Biodiesel from fresh oil treated with BHT (200, 600 and 1000 ppm)	0.86 ± 0.001	4.02 ± 0.04	0.09 ± 0.02
Biodiesel from WCO treated with BHT (200, 600 and 1000 ppm)	0.86 ± 0.001	4.04 ± 0.1	0.07 ± 0.01
Biodiesel from fresh oil treated with carvacrol (200, 600 and 1000 ppm) and with BHT : carvacrol = 1 : 1 (200 ppm each)	0.87 ± 0.001	4.14 ± 0.04	0.05 ± 0.01
Biodiesel from WCO treated with carvacrol (200, 600 and 1000 ppm) and with BHT : carvacrol = 1 : 1 (200 ppm each)	0.87 ± 0.001	4.24 ± 0.04	0.05 ± 0.003
Biodiesel from fresh oil treated with α-tocopherol (200, 600 and 1000 ppm) and with BHT : α-tocopherol = 1 : 1 (200 ppm each)	0.86 ± 0.0002	4.15 ± 0.1	0.06 ± 0.02
Biodiesel from WCO treated with α-tocopherol (200, 600 and 1000 ppm) and with BHT : α-tocopherol = 1 : 1 (200 ppm each)	0.87 ± 0.002	4.12 ± 0.04	0.05 ± 0.003

Biodiesel, in the absence of antioxidants, did not show oxidative stability due to the constant growth of the PV which was 89.5 mmol/kg on the fourth day. Figure 1 is representing the increasing oxidative stability dependant on the BHT concentration. The higher the antioxidant concentration, the lower the PV value. In the case of biodiesel from fresh oil, the increasing concentrations of BHT (200, 600 and 1000 ppm) resulted in decreasing PV (33.9 mmol/kg, 24.9 mmol/kg and 23.7 mmol/kg, respectively).

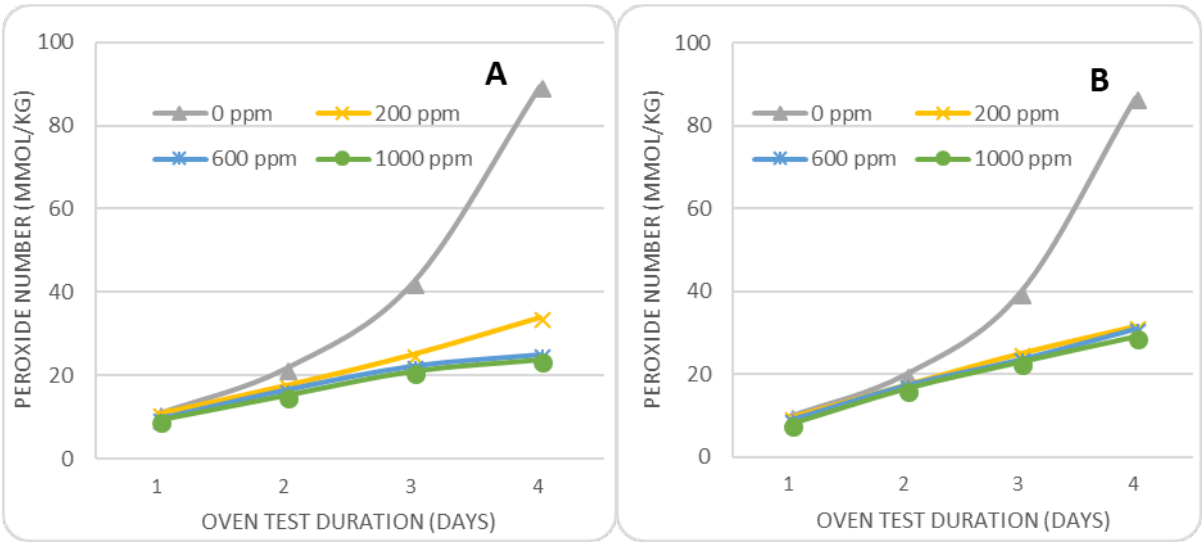

Figure 1. Peroxide value change in biodiesel from fresh (A) and WCO (B) after adding BHT compared to blank sample.

Our results are in line with the finding of Dunn [12] who also concluded that BHT is very effective in deteriorating oxidative degradation, especially at the concentration of 1000 pm. In general, increasing antioxidant concentration (up to 1000 ppm) shows sharp increases in activity followed by smaller increase in activity at higher concentration [5].

There has been a long-standing interest in the use of natural additives in fuels. Plant-based phenolic compounds such as tocopherols, carotenoids, xanthines, gallic acid, caffeic acid, vanillin, sinapic acid, p-coumaric acid, eugenol, sesamol, vanillic acid, cinnamic acid and resveratrol have antioxidant properties and are produced commercially on a large scale. A new

alternative to delay the biodiesel oxidative degradation process may be the use of natural antioxidants present in spices, bearing in mind that they do not damage the environment and are easily obtained [22]. Thus, herbal extracts of sage, rosemary, clove, allspice, thyme, cinnamon, oregano, marjoram, eucalyptus, artichoke, and turmeric have been identified as effective antioxidants in food products [23]. However, except for tocopherols, only very few studies have made on biodiesel fuels using these natural antioxidants. Beside tocopherol, curcumin is another example of a very promising antioxidant for biodiesel as it enhanced the stability of biodiesel by up to 83%. Further, it is not only cheaper and derived from natural substance, but also has potential to replace the synthetic antioxidant [24]. The study carried out by Mariuti and Bragnagnolo [25] reported several phenolic compounds that were isolated from oregano, including carvacrol, and demonstrated a great possibility of using spices as good antioxidants and possible substitutes for the synthetic antioxidants, especially in mixtures consisting of unsaturated carbon compounds as substrate. To the best of our knowledge, there is no research investigating carvacrol usage as means to increase oxidative stability of biodiesel. We chose carvacrol as a phenolic type antioxidant to analyse its influence on biodiesel, taking into account that it does exhibit significant antioxidant power in other samples.

According to our results, carvacrol is an antioxidant less effective in reducing the PV. In biodiesel synthesized from fresh oil, even the highest used concentration of carvacrol reduced the PV from 78.5 mmol/kg to only 48.5 mmol/kg. There is considerable evidence that phenolic antioxidants can be used in combination as they have synergistic activity and the collective effect of the two antioxidants is better than the sum of individual effects obtained when used separately [26]. In the case of carvacrol, its combination with BHT (1: 1, 200 ppm) proved to be insufficient, as well, the PV reaching only 42.5 mmol/kg.

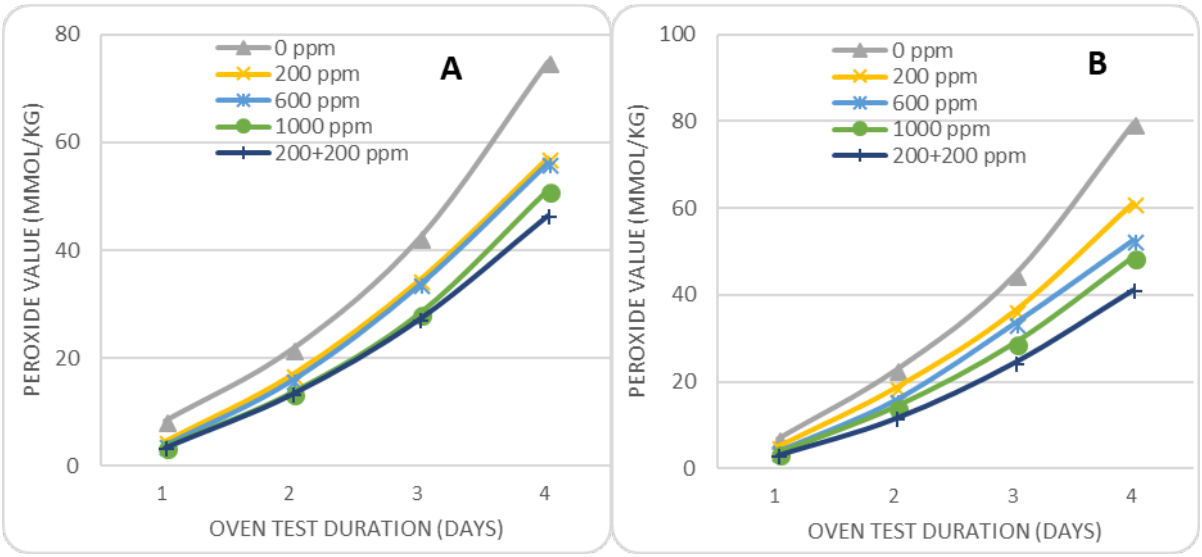

Figure 2. Peroxide value change in biodiesel from fresh (A) and WCO (B) after adding carvacrol and the combination of BHT and carvacrol compared to blank sample.

Samples from the last two biodiesel syntheses were treated with α-tocopherol (200, 600 and 1000 ppm) and a combination of BHT and α-tocopherol (1: 1, 200 ppm). Changes in the PV of all biodiesel samples are presented in Figure 3. Regardless of the antioxidant concentrations, the PV was not significantly reduced and it remained greater than 48 mmol/kg in all samples. It is also important to note that tocopherols are effective only if their concentration is approximately equal to their concentration in vegetable oils and at a higher level, they could act as a prooxidant. Most studies have reported that tocopherols have a limited antioxidant activity on biodiesel fuels when compared to synthetic antioxidants [4]. Our results are in line with that.

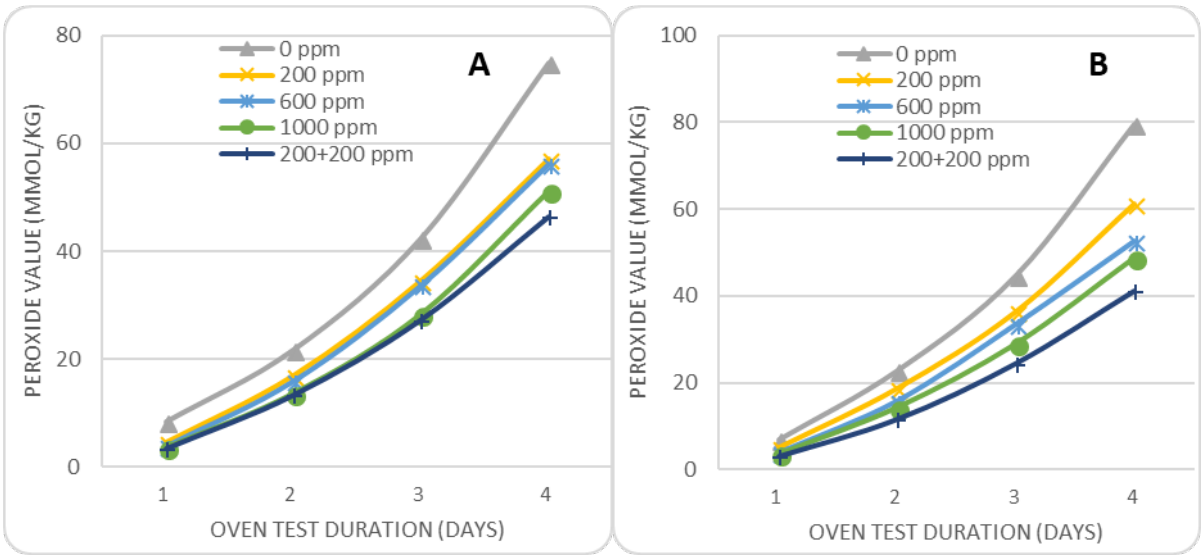

Figure 3. Peroxide value change in biodiesel from fresh (A) and WCO (B) after adding α-tocopherol and the combination of BHT and α-tocopherol compared to blank sample.

Enferadi et al. [21] also used α-tocopherol as an additive to biodiesel in order to reduce the PV. The antioxidant effect increased with concentration up to an optimal level. Above the optimal level, the increase in antioxidant effect with its concentration was relatively small. They established a threshold dose of 0.1 % α-tocopherol for stabilizing the biodiesel as the most economic dose, as well. The PV values obtained by Enferadi et al. [21] were lower than the PV in our work, which can be attributed to different conditions, materials and the use of freshly isolated α-tocopherol as opposed to the commercial products.

Of the three antioxidants used in this study, BHT proved to be the most effective antioxidant. During the oven test, a more pronounced rise in the PV is noticeable in the case of carvacrol and α-tocopherol compared to BHT. The PV exceeded 40 mmol/kg which is an indicator of ongoing biodiesel oxidation processes. The highest BHT concentration (1000 ppm) decreased the PV by four times. The lowest BHT concentration proved to be nearly as effective, decreasing the PV by its three-fold value. These results are valid regardless of the oil used for the biodiesel synthesis. Carvacrol and α-tocopherol increased the oxidative stability of the synthesized biodiesel, however to a lower extent than BHT. The effectiveness of the three antioxidants used is presented in Figure 4.

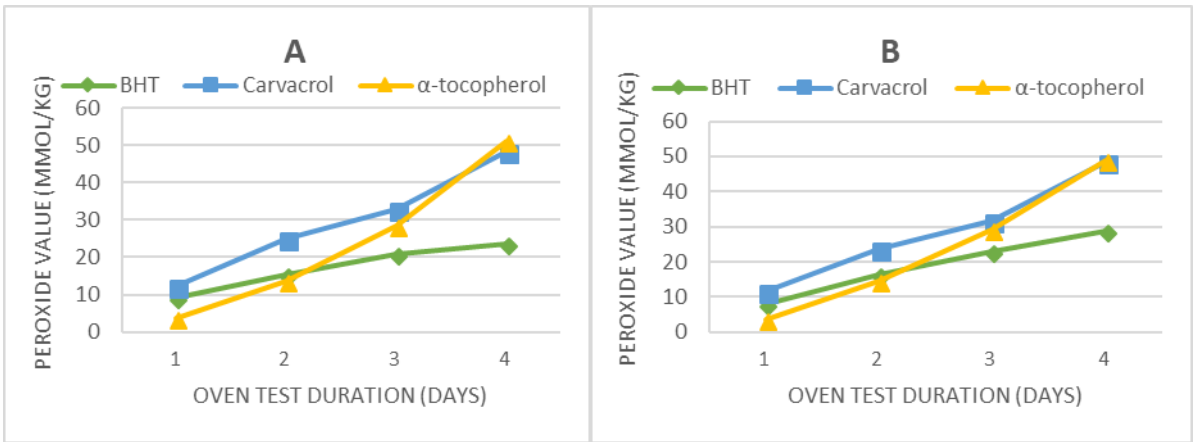

Figure 4. Comparison of the obtained PV of biodiesel synthesized from fresh (A) and WCO (B) in relation to the used antioxidant (1000 ppm).

While BHT is more expensive than the other two antioxidants, it is more efficient in ensuring a better biodiesel quality during storage and protecting the engines from damage that would be caused by fuel oxidation by-products.

3. Material and Methods

3.1. Chemicals

Used and unused sunflower oil was purchased from Bimal; calcium chloride, chloroform, potassium iodide and α-tocopherol from Semikem Sarajevo; potassium hydroxide from Distillation Teslic; sodium sulfate anhydrous from Zorka, Šabac; sodium thiosulfate pentahydrate from Kemika; glacial acetic acid (99-100%), 2% solution of phenolphthalein in alcohol; soluble starch;from Merck; ethanol, methanol, butylated hydroxy toluene and carvacrol from Sigma-Aldrich; distilled water. All chemicals were of analytical reagent grade.

3.2. Sample preparation

Biodiesel was produced in laboratory from fresh and waste sunflower oil. Although being edible oil, sunflower oil was chosen as a model raw material for testing the antioxidant additives because of its high degree of unsaturated fatty acids [27]. The waste oil was filtered and heated to 110-120 °C. After cooling the residual water was removed by adding sodium sulfate and the oil was filtered again.

3.3. Synthesis of biodiesel

Six biodiesel products were synthesized, three from fresh oil and three from waste oil, using the same apparatus. A methanolic solution of potassium hydroxide was used as a catalyst (oil/alcohol = 1/6 M ratio; mass of catalyst = 1% of oil mass). The oil and catalyst mixture were heated to 60 °C and stirred continuously on a magnetic stirrer for two hours. The reaction mixture was transferred to a separatory funnel and left overnight. The biodiesel was washed out by using distilled water in five portions. The extract was dried over anhydrous sodium sulphate, left overnight and filtered.

3.4. Characterization of oil and biodiesel

The characterization of oil and biodiesel was performed by determining the density, viscosity, AV, PV and the FP. The density was determined using a pycnometer of 25 ml, viscosity using the outflow velocity of fluids in capillary tubes at 40° C, the AV and PV by volumetric titrations and the FP using open device or the Marcusson flashpoint apparatus.

3.5. Schaal oven test

The oxidative stability of biodiesel was determined using the Schaal oven storage test. The biodiesel was divided in portions that were treated with various antioxidants of different concentrations, with the exception of one portion which was used as blank. The antioxidants BHT, carvacrol and α-tocopherol were used at the concentrations of 200, 600 and 1000 ppm, and added to the biodiesel portions at a ratio of 1:1. Such prepared samples were placed into the oven at a temperature of 60 ± 3 °C and monitored for changes in the PV over the period of 4 days.

4. Conclusions

Sunflower oil, fresh and waste cooking oil, have been used as a source for biodiesel synthesis. The reaction yield was min. 88 %. The biodiesel characterisation revealed that the measured parameters met the European (EN 14214) and American (ASTM D 6751) biodiesel fuel quality standards. Contrary to the density, viscosity and AV which were similar in biodiesel from both oil types, the PV was higher in waste oil. The PV was significantly reduced in the synthesized product. Based on the FP it can be concluded that the obtained biodiesel was free of residual methanol and other impurities. These findings suggest that fresh and WCO can be used as alternative raw material for biodiesel production. In order to stabilize the biodiesel against oxidative degradation BHT, carvacrol and α-tocopherol have been employed in various concentrations and their efficiency monitored by determining the PV over four days of the oven test duration. The efficiency was linear to the antioxidants' concentrations. While all antioxidants exhibited a certain increase in

oxidative stability, BHT at the concentration of 1000 ppm proved to be the most powerful and hence the most desirable antioxidant. The other quality parameters were neither influenced by biodiesel aging nor by the addition of antioxidants, even at the highest concentrations. Our results underline that both fresh and waste sunflower oil are valuable sources for producing biodiesel that meets quality standards, with the emphasis that WCO is bearing environmental and economic benefits. Further improvements that are related to enhancing oxidative stability can be accomplished using BHT at the concentration of 1000 ppm.

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