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COMPARISON OF BIODIESEL PRODUCTIVITIES OF DIFFERENT VEGETABLE OILS BY ACIDIC CATALYSIS*

Biodiesel has become a subject which increasingly attracts worldwide attention because of its environmental benefits, biodegradability and renewability. Biodiesel production typically involves the transesterification of a triglyceride feedstock with methanol or other short-chain alcohols. This paper presents a study of transesterification of various vegetable oils, sunflower, safflower, canola, soybean, olive, corn, hazelnut and waste sunflower oils, with the acidic catalyst. Under laboratory conditions, fatty acid methyl esters (FAME) were prepared by using methanol in the presence of 1.85% hydrochloric acid at 100 °C for 1 h and 25 °C for 3 h. The analyses of biodiesel were carried out by gas chromatography and thin layer chromatography. Also, biodiesel productivities (%) were determined on basis of the ratio of ester to oil content (w/w). The biodiesel productivities for all oils were found to be about 80% and about 90% at 25 and 100 °C, respectively. Also, the results showed that the yield of biodiesel depended on temperature for some oils, including canola, sunflower, safflower oils, but it was not found significant differences among all of the oil types on biodiesel productivities.

Key words: biodiesel; vegetable oils; acidic catalysis; transesterification; productivity.

Exploring new energy resources, such as biodiesel fuel, has gained importance in recent years. Biodiesel has recently become more attractive because of its environmental benefits. With recent increases in petroleum prices and uncertainties concerning petroleum availability, there is renewed interest in vegetable oil fuels for diesel engines [1]. In the European Union, biodiesel is by far the biggest biofuel and represents 82% of the biofuel production for 2003 [2].

The term of biodiesel refers to the alkyl monoesters of fatty acids produced from renewable feedstock, such as vegetable oils, with glycerin being the primary by product. Biodiesel production typically involves the transesterification of a triglyceride with methanol or other short-chain alcohols [3,4]. Through transesterification, high viscosity is reduced to a value closer to that of petrodiesel. Biodiesel can be used alone (B100), or more commonly as a 5 (B5) or 20% (B20) blend with petroleum-based diesel. The main advantages of biodiesel are its biodegradability, renewability, improved nontoxic exhaust emissions and higher lubricity properties [5]. Today, biodiesel is produced by catalysis of inorganic acids (HCl or H_2SO_4) [6,7], alkali (NaOH, KOH) [8-10] and free/immobilized lipases [11,12] with vegetable oils and short chain alcohols. Alkali and acidic catalysts are the most used catalysts for production of biodiesel because of having good performance and rate. Biodiesel production of alkali catalysts such as KOH and NaOH require anhydrous conditions. The presence of water leads to soap formation, which reduces the yield and causes difficulty in product separation [4,5]. This problem can be avoided by using acid catalysts such as sulfuric acid and hydrochloric acid. In recent years, the use of free or particularly immobilized lipases as catalyst for alcoholysis of oils has been widely investigated. But, enzymes as catalysts are limited in biodiesel production because of the fact that enzymes are more expensive and can lose some initial activity, and regeneration of enzymes is limited [13,14].

In recent years, a search for different catalysts for a sustainable transesterification process has been done. Recently, heterogeneous catalysts such as me-

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tal oxides, carbonates, zeolites and heteropolyacids have also been investigated for biodiesel production. Heterogeneous catalysts have the general advantage of being reusable and easy to separate from reaction products .In addition they are in general much more tolerant to water and FFAs in the feedstock. Therefore it does not lead to soap formation. However, heterogeneous catalyzed transesterifications require relatively elevated temperatures and pressures than those for homogeneous catalysts. Moreover one of the main problems with heterogeneous catalysts is their deactivation with time owing to many possible phenomena, such as poisoning, coking, sintering and leaching [15,16].

Various oils are used as raw materials for biodiesel production. Typical raw materials of biodiesel are rapeseed, soybean, palm and sunflower oils [17,18]. Waste cooking oil is also the source of feedstock. In this work, comparative studies on biodiesel productivity, effects of reaction temperature and the contents of fatty acids (FA) in oils were presented. Experiments were performed by using 1.85% HCl catalyst in methanol for 1 h at 100 °C and 3 h at 25 °C. FAMEs in the biodiesel were analyzed by gas chromategraphy. Then the conversion rate (%) to biodiesel of the eight vegetable oils we used, the contents of FA in oils and the temperature effect on productivity were investigated.

EXPERIMENTAL

Materials

Crude vegetable oils such as sunflower, corn and canola oils were obtained from Olin Oil Factory in Edirne, Turkey. Refined safflower oil, soybean oil, crude hazelnut oil and crude olive oil were obtained from the manufacturers of Nigde, Adana, Ordu and Aydın, Turkey, respectively. Waste cooking sunflower oil was obtained from the authors' university canteen. TLC plate, molecular sieve 4A, iodine, methanol, HCl, *n*-heptane, petroleum ether, diethyl ether, acetic acid, oleic acid, linoleic acid, β-carotene, oleic and linoleic acid methyl esters were purchased from Merck and Sigma-Aldrich.

Properties of the used oils

The oil densities were determined by using the standard method ASTM D7042.

The oil viscosities were determined by using an A&D's vibro viscometer.

For determination of the oil pH, 2 g of the oil sample was poured into a clean dry 25 ml beaker and 25 ml of hot distilled water was added and stirred slowly. Then it was cooled in a water bath to 25 °C. After the pH electrode was standardized with buffer solution, it was immersed into the diluted sample and the pH value was measured.

Determination of fatty acid compositions in the oils

The fatty acid content of vegetable oils was analyzed using a model 6890N Agilent-GC gas chromatography with a DB-23 capillary column and a flame ionization detector (FID). Five microliters of the sample and 300 μl of 1.4 mmol/l heptadecanoic acid methyl ester (*n*-heptane as the solvent) which served as the internal standard were precisely measured and mixed thoroughly. Samples were injected by a sampler at an oven temperature of 50 °C, and the GC oven was heated at 15 °C/min to 250 °C and then held for 6 min. Nitrogen was the carrier gas.

Preparation of the catalyst

Transesterification is carried out with the acidic reagent that is 1.85 % (w/v) hydrogen chloride in dry methanol. The methanol was dried on silica molecular Sieve 4A and cooled in deepfreeze. The 2.5 ml of cons. HCl (37%, d = 1.19 g/ml) was taken and dissolved into 50 ml of cool-dry methanol.

Preparation of the oils for biodiesel production

The oils were filtered to remove any of the debris present. The oils were heated to 100 °C for 20 min to evaporate the water present in the oils. A hot plate with magnetic stirrer was used for heating. Then, the temperature of oils was brought down to room temperature.

Procedure for the transesterification reaction

The acidic catalyst and oils prepared as above were mixed and put in a reaction flask with connection reflux condenser and then the mixture was stirred vigorously for 1 h at 100 °C. After every 20 min the temperature of the mixture was gradually raised from 10 up to 100 °C, then the reaction was carried out for 1 h. After the reaction time was over, the mixture was transferred to a separatory funnel and it was put aside for a day to separate ester phase and glycerin phase.

Excess methanol, catalyst and glycerin produced during the reaction were removed from methyl esters by washing with distilled water. The ester phase was placed in the separation funnel. Water was sprayed onto the top of the funnel at a low speed. For complete settling of water, 24 h were required. Furthermore, the transesterification reaction was carried out again by using all of the oils at 25 °C for 3 h.

After the fatty acid methyl esters (FAME) production, conversion ratios of oils to biodiesel were de-

termined on the basis of the ratio of obtained methyl ester amounts to used oil amounts (w/w) and described as biodiesel productivity (%).

Analysis of fatty acid methyl ester

The qualitative analysis of the yield was carried out on silica gel plate with TLC. Petroleum ether:diethyl ether:acetic acid (8:3:0.2) was used as mobile phase. After 30 min, the plate was dried at 110 °C and then colored in iodine chamber for all of the oil varieties.

For the quantitative analysis, the methyl esters in the biodiesel were diluted into *n*-heptane and GC analyses were performed with model 6890N Agillent GC as "Determination of fatty acid compositions in the oils" section.

RESULTS AND DISCUSSION

GC analysis of the oils

Table 1 summarizes the fatty acid composition of used vegetable oils as well as pH, viscosity and density values. The kinds and amounts of fatty acids in oils were measured by gas chromatography. The fatty acids which were commonly found in vegetable oils were palmitic (16:0), stearic (18:0), oleic (18:1), linoleic (18:2) and linolenic (18:3). According to the results it was observed that the hazelnut, olive and canola oils contained higher percentages (78.0, 74.7 and 63.0%, respectively) of oleic acid when compared to the others, and the safflower, waste sunflower, sunflower, corn and soybean oils contained higher percentages (72.3, 59.6, 58.5, 58.4 and 56.2%, respectively) of linoleic acid. The fatty acid content of oils was generally unsaturated (18:1 and 18:2) fatty acids rich according to GC analysis.

Conversion ratios of oils to biodiesel and effect of temperature

Biodiesel productivities of different vegetable oils by using acidic catalyst at the 25 and 100 °C are shown in Table 2. As it is seen in the table, biodiesel productivity was averaged between 81-86% at 25 °C and 83-95% at 100 °C by acidic catalyst in the study. The biodiesel productivities depending on temperature have increased between 1-16% and also the highest increase depending on temperature was found in canola oil with 15.9%.

The fatty acid methyl ester (FAME) profile of biodiesels produced in the study is shown in Table 3. And also, TLC image of produced biodiesels and standards is displayed in Figure 1.

The parameters affecting biodiesel productivity are reaction temperature, pressure, molar ratio, water content, FFA content, catalyst type and concentration [3,4,19,20]. Temperature, especially, plays an impor-

Table 1. GC analysis of fatty acids, pH, density and viscosity values in the vegetable oils

Vegetable oil	Fatty acid content, %								pH (25 °C)	Density, g/ml (25 °C)	Viscosity, mPa s(40 °C)
	14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:0			
Safflower	0.30	7.3	0	1.9	13.6	72.3	0	0.3	6.78	0.922	23.4
Soybean	0	13.9	0.3	2.1	23.2	56.2	4.3	0.16	6.88	0.920	23.1
Sunflower	0.08	6.1	0.12	3.7	30.1	58.5	0.11	0.23	6.02	0.918	23.6
Canola	0	4.74	0.19	1.80	63.0	19.8	7.88	0	5.85	0.929	25.3
Corn	0.26	10.8	0.08	2.23	26.1	58.4	0.91	0.43	6.63	0.916	24.8
Olive	0.40	5.0	0.32	1.68	74.7	17.6	0	0.80	6.96	0.909	25.6
Hazelnut	0.1	5.2	0.3	2.1	78.0	13.8	0.3	0.1	6.75	0.919	26.7
Waste sunflower	0	5.8	0.1	3.82	30.6	59.6	0.10	0.20	5.36	0.915	24.6

Table 2. Biodiesel productivities of used vegetable oils by acidic catalysis

Vegetable oil	Biodiesel productivity, %		Productivity increase with temperature, %
	25 °C	100 °C	
Safflower	84.7	94.3	11.3
Soybean	85.9	94.2	9.7
Sunflower	83.4	95.2	14.1
Canola	80.8	93.7	15.9
Corn	83.2	83.3	0.1
Olive	84.3	85.3	1.2
Hazelnut	82.5	83.4	1.1
Waste sunflower	84.3	90.4	7.2

Table 3. GC results of fatty acid methyl ester of produced biodiesels by acidic catalysis

Vegetable oil	FAME composition of biodiesel, %									
	14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:0	24:0	Others
Safflower	0.21	6.68	0	2.05	17.88	70.36	0.62	0.34	0	0.28 (22:0)
Soybean	0.18	0	11.07	4.08	23.70	51.84	7.32	0.37	0	1.19 (22:0)
Sunflower	0.32	6.67	0.17	3.65	28.64	57.63	0.48	0.23	0	0
Canola	0.23	5.46	0.32	1.98	61.64	19.27	7.76	0.29	0	1.36 (23:0)
Corn	0.15	14.33	0.19	1.92	28.26	53.07	0.21	0.21	0	0.45 (23:0)
Olive	0.10	6.90	0.43	2.20	57.93	19.25	6.84	0.42	0	0.58(22:0) 4.14 (23:0)
Hazelnut	0.49	6.19	0.20	2.00	75.36	14.83	0.22	0	0	0.73(23:0)
Waste sunflower	0.22	10.90	0.16	3.87	28.44	54.75	0.16	0	0	0

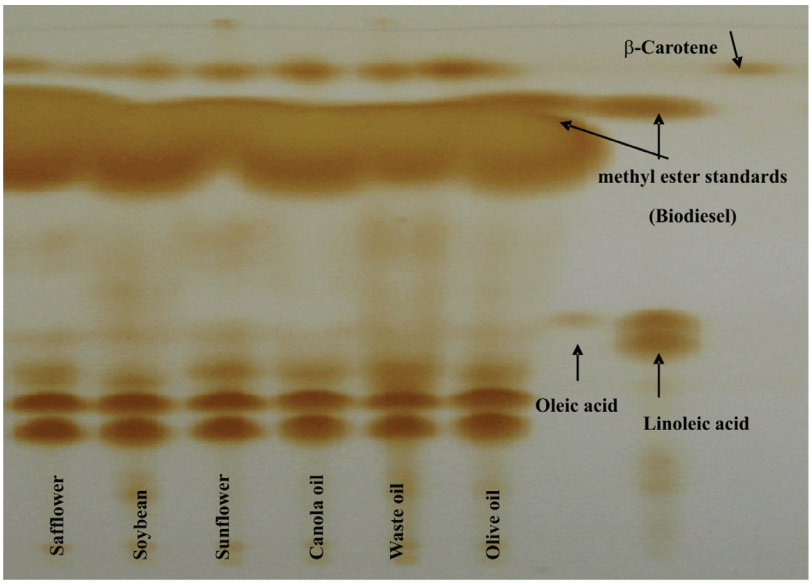

Figure 1. TLC images of produced biodiesels and standards by acidic catalysis.

tant role in the synthesis of biodiesel. The transesterification reaction can be conducted at various temperatures ranging from room temperature to different high temperatures [21,22]. At higher temperature, the extent of phase separation decreases and the reaction rate increases, and also the time required to reach maximum conversion decreases [5,15]. However, it was observed that the reaction will proceed to near completion even at ambient temperature if given enough time [23].

As seen in Table 2, when the temperature was increased from 25 to 100 °C, the biodiesel productivity increased in some oils. It was observed that increasing the reaction temperature had a favorable influence on the yield of ester conversion on canola (15.9%), sunflower (14.1%), safflower (11.3%) and soybean (9.7%) oils, especially.

Previous works on transesterification using acid catalyst reported that methyl ester content was 92% at 100 °C in 4 h for soybean oil [24], and 97.5% at 110 °C in 2 h for waste cooking oil [25], similarly to our results. In the study of Refaat *et al.* [22], the yields of transesterification reaction of waste vegetable oil were as 95.79% (at 65 °C) and 71.74% (at 25 °C) by using alkali catalyst after 1 h of reaction, and for neat vegetable oil were as 96.15% (at 65 °C) and 75.40% (at 25 °C) under the same conditions. Also, their results indicated that by increasing the reaction time from 1 to 3 h at 65 °C, no noticeable increase in the yield was detected.

Effect of vegetable oil type

Various vegetable oils have been used for synthesis of methyl esters by using acidic catalyst in the present study. Table 3 shows the FAME profiles (%) of used oils that are obtained by GC. Free fatty acid (FFA) content and structure of oils have an influence on the biodiesel production. If FFA concentration of the feedstock is higher, the alkali catalyst should not be used in the transesterification reaction due to the soap formation [3]. The acidic catalyst is much more tolerant to FFAs and is not strongly affected by the presence of the free fatty acids in the feedstock [5].

Moreover, the fatty acid chain composition of the triglyceride in the feedstock, such as its length or degree of unsaturation, has important effects on the characteristics of biodiesel. Esters with polyunsaturated fatty acid chains are less stable than saturated fatty acid chains as a result of relatively fast oxidation during storage [3]. Biodiesel made from feedstocks containing higher concentrations of high melting point saturated long fatty acid chains tends to have relatively poor cold flow properties [16]. Furthermore, impurities present in the feedstock also affect the quality of the biodiesel. The conversion levels into esters using refined vegetable oils can be higher than using crude vegetable oils under the same condition [18].

In the study, the biodiesel productivities (%) of oils rich in linoleic acid (18:2), such as safflower and soybean, were slightly higher than those of oils rich in oleic acid (18:1), such as olive and hazelnut. Nevertheless, according to Table 2, the biodiesel productivities were not found significantly different among all of the oil types, and also between refined and crude oils.

Generally, the conversion of oils into biodiesel through the transesterification process resulted approximately similar in comparison with waste cooking oil and other vegetable oils. Therefore, we can say that waste cooking oil is available with a relatively cheap price for biodiesel production versus vegetable oil costs. In addition performance and exhaust emission tests with biodiesel derived from used cooking oils are similar to properties that of biodiesel derived from other vegetable oil feedstock [15].

CONCLUSION

Biodiesel has recently become more attractive because of its environmental benefits and the fact that it is made from renewable resources. In this research, eight fatty materials were transformed into biodiesel by transesterification reaction with methanol by using acid catalyst. Contents of FFAs in oils, the effects of reaction temperature and types of oils on productivity of production biodiesel from seven different of vegetable oils and a waste cooking oil by acidic catalyst were compared. TLC image and GC analysis showed that biodiesel productivities were not found significantly different for the oil types. The increases of biodiesel productivity depending on temperature were between 1.0-15.9% for all of the oils. Therefore, it can be recommended to perform the reaction at room temperature to reduce the cost of biodiesel production with the acidic catalyst method. In addition, compared to other refined or unrefined vegetable oils, using the waste cooking oil for biodiesel production provides low-cost and environmental advantages.

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REFERENCES

[1] A. Demirbas, Energy Convers. Manage. **50** (2009) 14-34

[2] EBB (Europan Biodiesel Board) (2007) EBB official press release: 2006, 2007 production and capacity statistics, http://www.ebb-eu.org [accessed 3 January 2010]

[3] M. Canakci, H. Sanli, J Ind. Microbiol. Biotechnol. **35** (2008) 431-441

[4] F. Ma, M.A. Hana, Bioresour. Technol. **70** (1999) 1-15

[5] E. Lotero, Y. Liu, D.E. Lopez, K. Suwannakarn, D.A. Bruce, J.G. Goodwinn, Ind. Eng. Chem. Res. **44** (2005) 5353-5363

[6] B. Liu, Z.Zhao, J Chem. Technol. Biotehnol. **82** (2007) 775-780

[7] F. Ataya, M.A. Dube, M. Ternan, Energy&Fuels **21** (2007) 2450-2459

[8] D.Y.C. Leung, Y. Guo, Fuel Process. Technol. **87** (2006) 883-890

[9] J.M. Dias, M.C.M. Alvim-Ferraz, M.F. Almeida, Fuel **87** (2008) 3572-3578

[10] X. Meng, G. Chen, Y. Wang, Fuel Process. Technol. **89** (2008) 851-857

[11] N. Dizge, B. Keskinler, A. Tanriseven Biochem. Eng. J. **44** (2009) 220-225

[12] A.B.R. Moreira, V.H. Perez, G.M. Zanin, H.F. Castro, Energy Fuels **21** (2007) 3689-3694.

[13] A. Salis, M. Pinna, M. Monduzzi, V. Solinos, J. Biotechnol. **119** (2005) 291-299.

[14] Y. Wu, W. Du, J. Zeng, D. Liu, Biocatal. Biotransform. **22** (2004) 45-48

[15] A.A. Refaat, Int. J. Environ. Sci. Tech. **7** (2010) 183-213

[16] A. Sivasamy, K.Y. Cheah, P. Fornasiero, F. Kemausuor, S. Zinoviev, S. Miertus, Chem. Sus. Chem. **2** (2009) 278--300

[17] A. Demibas, Energy Convers. Manage. **44** (2003) 2093--2109

[18] R. Jothiramalingam, M.K. Wang, Ind. Eng. Chem. Res. **48** (2009) 6162-6172

[19] J.M. Marchetti, V.U. Miguel, A.F. Errazu, Fuel Process. Technol. **89** (2008) 740-748

[20] A. Srivastava, R. Prasad, Renew. Sust. Energ. Rev. **4** (2000) 111-133

[21] D.A.G.Aranda, R.T.P. Santos, N.C.O.Tapanes, A.L.D. Ramos, O.A.C.Antunes, Catal. Lett. **122** (2008) 20-25

[22] A.A.Refaat, N.K.Attia, H.A.Sibak, S.T. El Sheltawy, G.I. El Diwani, Int. J. Environ. Sci. Tech. **5** (2008) 75-82

[23] B. Freedman, E.H. Pryde, T.L. Mounts, J. Am. Oil Chem. Soc. **6** (1984) 1638-1643

[24] X. Miao, R. Li, H. Yao, Energy Convers. Manage. **50** (2009) 2680-2684

[25] C. Komintarachat, S. Chuepeng, Ind. Eng. Chem. Res. **48** (2009) 9350-9353

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NAUČNI RAD

POREĐENJE PROIZVODNJE BIODIZELA IZ RAZLIČITIH BILJNIH ULJA KISELOM KATALIZOM

Biodizel je postao predmet istraživanja koji sve više privlači pažnju širom sveta zbog ekoloških pogodnosti, biodegradabilnosti i obnovljivosti. Tipična proizvodnja biodizela uključuje transesterifikaciju sirovine koja sadrži trigliceride sa metanolom ili drugim alkoholima sa kratkim lancem. U ovom radu prikazani su rezultati transesterifikacije različitih biljnih ulja: suncokreta, šafranike, kanole, soje, masline, kukuruza, lešnika, kao i otpadnog suncokretovog ulja, u prisustvu kiselog katalizatora. Metil-estri masnih kiselina su dobijeni u laboratorijskim uslovima koristeći metanol i 1,85 % hlorovodonične kiseline na 100 °C za 1 h ili na 25 °C za 3 h. Biodizel je analiziran gasnom i tankoslojnom hromatografijom. Produktivnost procesa je određena na bazi odnosa etstara i ulja. Prinos biodizela za sva ulja je bila oko 80% na 25 °C, a 90% na 100 °C. Takođe, dobijeni rezultati su pokazali da prinos biodizela iz nekih ulja (kanola, suncokret i šafranika) zavisi od temperature, ali nisu utvrđene značajne razlike između prinosa biodizela iz svih ulja.

Ključne reči: biodiezel; biljna ulja; kisela kataliza; transesterifikacija; produktivnost.