BAHÇE 52(1): 1-6 (2023)
https://doi.org/10.53471/bahce.1085986

FATTY ACID COMPOSITION AND BIODIESEL QUALITY OF *Brassica nigra*, *Brassica napus* and *Sinapis arvensis* SEEDS

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Geliş Tarihi / Received: 10.03.2022 *Kabul Tarihi / Accepted: 28.12.2022*

ABSTRACT

The increasing world population and developing industrial areas increase the need for energy. This situation makes alternative and renewable energy sources and the efficient use of these sources more valuable. In this study, the seeds of *Sinapis arvensis*, *Brassica nigra*, and *Brassica napus* from *Brassicaceae* family grown in ecological conditions of Bayburt province of Türkiye, to determine the usability potential of wild species in biodiesel production. Biodiesel quality characteristics and fatty acid composition were determined for the first time for the region using GC-MS. The oil yield of the species included in the study from the *Brassicaceae* family was found to be between 30.29% and 46.02%. In addition, linolenic acid (7.62-13.70%) values were determined the lowest in *Brassica napus* and the highest in *Brassica nigra*. In terms of flash point (194-195°C), *B.napus* and *S.arvensis* were the closest species. Fatty acid composition and biodiesel quality analysis results of *S.arvensis* and *B.nigra* were similar to *B.napus*. It has been observed that the wild species *S.arvensis* and *B.nigra* have renewable energy production potential in terms of biodiesel quality characteristics and fatty acid composition.

Keywords: Bioenergy, *Brassica napus*, *Brassica nigra*, fatty acid, green energy, *Sinapis arvensis*

FARKLI YABANİ BRASSICA TOHUMLARININ YAĞ ASİDİ KOMPOZİSYONU VE BİYODİZEL KALİTESİ

ÖZ

Her geçen gün artan dünya nüfusu ve gelişen sanayi alanları enerjiye duyulan ihtiyacı da artırmaktadır. Bu durum alternatif ve yenilenebilir enerji kaynaklarını ve bu kaynakların verimli kullanımı konusunu daha değerli kılmaktadır. Bu çalışmada, yabani türlerin biyodizel üretiminde kullanılabilirlik potansiyelini belirlemek amacı ile Türkiye'nin Bayburt ili ekolojik koşullarında yetiştirilen *Brassicaceae* familyasından *Sinapis arvensis*, *Brassica nigra* ve *Brassica napus* tohumlarının biyodizel kalite özellikleri ve GC-MS kullanılarak yağ asitleri kompozisyonu bölge için ilk kez belirlenmiştir. *Brassicaceae* familyasından çalışmada yer alan türlerin yağ verimi %30.29-46.02 arasında bulunmuştur. Ayrıca linolenik asit (%7.62-13.70) değerleri en düşük *B.napus*, en yüksek *B.nigra*'da belirlenmiştir. Parlama noktası bakımından (194-195°C) *B.napus* ve *S.arvensis* birbirine en yakın türler olduğu görülmüştür. *S.arvensis* ve *B.nigra*'nın yağ asidi kompozisyonu ve biyodizel kalite analiz sonuçları *B.napus*'a benzer değerlerde bulunmuştur. Yabani türler olan *S.arvensis* ve *B.nigra*'nın biyodizel kalite özellikleri ve yağ asitleri kompozisyonu bakımından yenilenebilir enerji üretim potansiyeline sahip olduğu görülmüştür.

Anahtar Kelimeler: Biyoenerji, *Brassica napus*, *Brassica nigra*, yağ asitleri, yeşil enerji, *Sinapis arvensis*

INTRODUCTION

Brassicaceae (*Cruciferae*) family contains many species of economic importance. This family, represented by 338 genera and 3709 species in the world, has 85 genera and 567 taxa in Türkiye [1, 3]. It is known that there are still many species that should be investigated even if researches are made about wild species belonging to *Brassicaceae* family [4].

The *Brassicaceae* includes many edible and industrial fodder crop, oilseed, condiment species and vegetables. In addition, leafy brassicas are grown to supplement the low pasture growth in dry summers [5]. This family attracts attention especially with the variety of oilseed species. Canola or oilseed rape (*Brassica napus* L.) is the most important oil crop that use for biofuel of the family [6]. Additionally, *Camelina sativa* (L.) Crantz, *Crambe hispanica* L. subsp. *abyssinica* (Hochst. ex R.E.Fr.) Prina, *Eruca*

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vesicaria (L.) Cav. and *Brassica carinata* A. Braun are using for obtained the biodiesel, too [7, 9].

Oil crops and their lipid yield are gain the significance because crude lipid is the most important needs of countries in recent years. Fatty acid compositions show the quality of lipid and oil crops. For definated the quality of oil crops, lipid yield and fatty acid compositions should be determined. *Brassica napus* (L.) W.D.J.Koch., *Brassica nigra*, *Sinapis arvensis* L. are important plants for about their lipid yield and fatty acid compositions [3].

The world population, which is increasing day by day, increases its energy need. This necessitates the existence of alternative energy sources. Some species that belongs to Brassicaceae family have the potential to be used as biofuels energy. Determination and cultivation of these species become more important day by day [10]. Recently, plant oils are frequently used in biodiesel production. This increases the importance of oilseed plants [11].

Biodiesel is a renewable alternative energy source that has expanded its use area in recent years. Especially the biodegradability, low emissions and production from non-toxic raw materials such as vegetable and animal oil are among the reasons why biodiesel is preferred [9,12]. Several types of vegetable oils can be used for the preparation of biodiesel especially rapeseed (*Brassica napus* L.) is the important plant which is growing for this [13].

Some Brassica spp. are used for producing biofuels. *B.napus* is only plant for biodiesel in Türkiye. There is a gap for producing biofuel from plants in Türkiye and wild Brassica spp. have potential for using as biofuel plants as known. [14]. The studies are show that some Brassica spp. can be an alternative to production the biodiesel. The aim of this study is to realize the production of biodiesel using six different Brassica local breeds and determine the lipid yield and quality parameters according to standards of biodiesel which has started to be used in many countries.

MATERIALS AND METHODS

Plant Material

In this study, seeds of *Sinapis arvensis*, *Brassica nigra* and *Brassica napus* from *Brassicaceae* family were used as material. Because of *B.napus* is a culture plant, it was provided from commercial seed. Seeds of *Sinapis arvensis* was collected from natural habitat of Istanbul and Tekirdag Province. In addition, seeds of *Brassica nigra* were collected from three different locations from Edirne province. Three different species and six local breeds of *Brassicaceae* family were cultivated in the experiment field of Bayburt University with four replications according to Randomized Blocks Experimental Design under ecological condition of Bayburt region of Türkiye. The soil of experimental field was analyzed by the way of taken from 0 to 30 cm depth according to the method reported by Page et al. [15] were determined the includes of texture, pH, NaCl, $CaCO_3$, organic matter, P_2O_5 and K_2O. The result of analysis of soil sample is given Table 1.

Table 1. The soil sample analysis results
Çizelge 1. Toprak numunesi analiz sonuçları

Depth (cm)	Texture	pH	NaCl (%)	$CaCO_3$ (%)	Organic Matter (%)	P_2O_5 (kg da^{-1})	K_2O (kg da^{-1})
0-30	Clayey	7.75	0.05	9.30	0.99	11.44	80.30

Determination of Lipid Yield and Fatty Acids Composition

For lipid extraction, the Brassica spp. seeds were milled and placed in the extractor section of the soxhlet apparatus (Buchi B-811) and extracted with hexane for an average of four hours. After extraction was completed, hexane was removed from the resulting lipid. Fatty acid methyl esters were prepared and fatty acid composition was determined. The fatty acids composition of the Brassica spp. seeds was determined using GC-MS. For the preparation of fatty acid methyl esters 100 mg of the resulting lipid is dissolved with 10 mL of hexane. 100 µL of 2N methanolic potassium hydroxide is added and after vortexing for 30 s and centrifuged. At the end of the centrifugation, 1 ml of supernatant is taken and fatty acid analysis is performed on GC-MS [16]. DB-23 60 m × 0.25 mm ID, 0.15 µm (J&W 122-2361) column and helium will be used as carrier gas. In addition, the YAME (methyl esters) and LAME (linolenic acid methyl ester) analysis were carried out on GC device according to TS EN 14103 and fatty acid composition analysis were carried out according to TS EN ISO 12966 types.

Biodiesel Quality Analysis

In order to determine the biodiesel quality analysis, biodiesel was obtained using transesterification method from the plants used in this study and measurements were made at different parameters. In this content; ester content, linolenic acid content, water determination, kinematic viscosity and flash point were determined. These parameters were determined in the laboratory by the procurement of services from Republic of Türkiye Ministry of Agriculture and Forestry Black Sea Agricultural Research Institute. The ester and linolenic acid methyl ester content were determined according to TS EN 14103: 2011, TS 6147 EN ISO 12937 was used for water determination and TS 1451 EN ISO 3104 standard was used for determination of kinematic viscosity. In addition, flash point determination was made according to TS EN ISO 2719 quality standards [17].

Statistical Analysis

For statistical analysis, SPSS 25.0 statistical software were used. Mean and standard deviation were performed.

RESULTS AND DISCUSSION

Lipid Yield and Fatty Acids Composition

In this study, lipid yield and fatty acid compositions of different *Brassicaceae* local breeds were determined. Lipid yield of the plants are given in the Figure 1. The highest lipid yield level was seen in *Brassica napus* although the least lipid yield level was seen in *B.nigra*. The results of lipid yield for *B.napus* were higher than the results of some other studies, [17, 18] and consistent with some results of from the literature, Oz [19]. (43.46-47.6%), Tan [20], (12.31-46.47%), Rayati et al. [21] (26.35-59.18%). The differences between the results of the researches could be caused by eco-geographical differences or the variation of the seeds. The lipid yield of *Sinapis arvensis* was determined the higher value from the study that made by researchers [22, 23]. When the lipid yield of *B.nigra* was examined, it was seen that higher results were obtained than [24]. It could be because of differences growth conditions or watering methods. Oil content of plants are affected from ecological condition of growing area. Especially amount of rain or soil condition is so important for fatty acid composition and oil yield. Because of this, the area which uses for grown oil crops is so important and should be choose correctly.

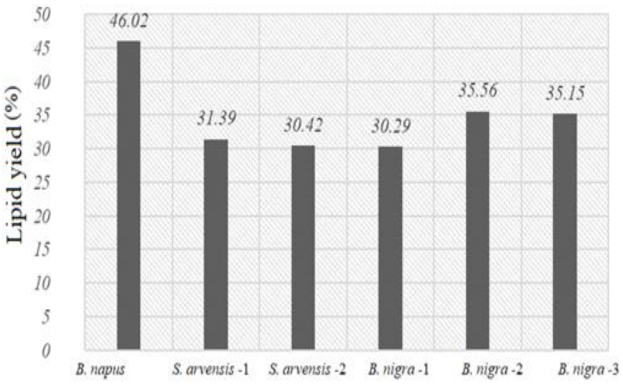

Figure 1. Lipid yields of the *Brassicaceae* local breeds

Şekil 1. Brassicaceae yerli ırklarının yağ verimleri

According to fatty acid composition, oleic acid is the major fatty acid for *B.napus*. In addition, erucic acid is the major fatty acid for *S.arvensis* and *B.nigra*. The differences were caused by plants to be culture or wild form is thought to be. When the fatty acid composition of the local breeds was determined, palmitic and stearic acids were similar with *B.napus* and other local breeds. On the other hand, oleic acid values were difference at 11.16-62.07%. The reason this wide range is differences of species and local breeds. Although species and local breeds which were used in this study are similar, they have different fatty acids and it is to be expected. All values of fatty acid composition are shown in Table 2.

Table 2. The fatty acid composition of *B.napus, B.nigra* and *S.arvensis*

Çizelge 2. B.napus, B.nigra ve Sinapis arvensis'in yağ asidi kompozisyonu

Fatty Acid (%)	*B.napus*	*S.arvensis-1*	*S.arvensis-2*	*B.nigra-1*	*B.nigra-2*	*B.nigra-3*
Palmitic acid	4.66±1.19	3.03±0.44	3.09±0.38	3.42±0.05	3.45±0.02	3.16±0.31
Stearic acid	1.52±0.15	1.14±0.23	1.17±0.20	1.41±0.04	1.54±0.17	1.47±0.10
Oleic acid	62.07±41.4	11.16±9.49	11.48±9.17	13.10±7.55	13.05±7.60	13.05±7.60
Linoleic acid	20.57±4.75	14.15±1.67	14.02±1.80	16.04±0.22	15.56±0.26	14.57±1.25
Linolenic acid	8.89±4.93	13.75±0.07	13.81±0.01	15.12±1.30	15.37±1.55	15.98±2.16
Arachidic acid	0.53±0.53	0.78±0.28	0.80±0.26	1.37±0.31	1.45±0.039	1.42±0.36
Eicosanoic acid	1.19±8.89	13.49±3.41	13.96±3.88	10.66±0.58	10.81±0.73	10.35±0.27
Behenic acid	0.26±0.16	1.33±0.94	1.34±0.24	1.17±0.07	1.20±0.10	1.29±0.19
Erucic acid	0.32±31.72	40.78±8.83	39.81±7.74	36.84±4.80	36.63±4.59	37.84±5.80
Lignoceric acid	0.00±0.61	0.53±0.08	0.53±0.08	0.85±0.24	0.87±0.26	0.85±0.24

Erucic acid values was found between 36.63-37.84% for *Brassica nigra* moreover between 39.81-40.73% for *Sinapis arvensis*. The results of erucic acid values were similar with Mandal et al. [24] but higher than Ozcan et al. [22], Tonguc & Erbas [23]. The content of linolenic acid of *B.napus* is suitable for the standards but the other local breeds which were studied in this research, are higher than the standard. In additionally the results of linolenic acid values were found similar to some other studies [25, 28]. Generally, the results similar with the older studies but there are some differences, too. Ecological conditions are so important for fatty acids. It is thought that, differences can be caused by eco-geographical conditions.

Biodiesel Quality Characteristics

Within the scope of quality analysis, biodiesel was obtained from *Brassica napus*, *Sinapis arvensis* and *B.nigra* seeds by transesterification method. This biodiesel determined ester content, linolenic acid content, water determination, kinematic viscosity determination, and flash point determination. Production of biodiesel from seeds and the quality analysis were made by Republic of Türkiye Ministry of Agriculture and Forestry Black Sea Agricultural Research Institute by using procurement of services. The results of the biodiesel quality analysis are shown in Table 3.

Brassica napus is known as the biodiesel plant so the results of biodiesel quality analysis are important for this plant [29]. Therefore, the similarity of results of *B.napus* with other plants that were used in this study is also important. According to the results of biodiesel quality analysis, value of ester, linolenic acid, water determination, kinematic viscosity determination and flash point determination for *B.napus* are found respectively 86.99%, 7.62%, 249 mg kg^{-1}, 4.98 mm^{2}s^{-1}, 195°C. Viscosity has great importance for the use of diesel fuels. Because the viscosity of the fuel is an important feature in terms of lubrication of the fuel system. The viscosity measurement of the European Biodiesel standard that accepted by our country should be measured by TS EN 14214 standard, and the result should be between 3.5 and 5 mm^2 sec^{-1}. However, according to the norm of the American Petroleum Institute ASTM D 445, the viscosity values should be 1.9 to 6 mm^2 sec^{-1} [16]. According to the kinematic viscosity results, *B.napus* complies with European biodiesel standards, *Sinapis arvensis* and *B.nigra* are in compliance with American biodiesel standards.

The ester content for the local breeds used in this study was found to be between 86.99% and 95.99%. The obtained ester content values are close to some studies but not identical with them [18]. In the biodiesel analysis obtained, water content values were ranged from 231 mg kg^{-1} to 306 mg kg^{-1}. However, these values found parallel with many similar studies [30, 36] but different from the others [37]. According to results; in addition to similarities with other studies, differences were found too, this situation could be because of eco-geographical conditions of the variability of local breeds.

Table 3. The result of biodiesel quality analysis is given as average ± standard deviation and mean value
Çizelge 3. Biyodizel kalite analizi sonucu ortalama ± standart sapma ve ortalama değerler

Local Breeds	Ester Content (%)	Linolenic Acid Content (%)	Water Determination (mg kg^{-1})	Kinematic Viscosity Determination (mm^2 s^{-1})	Flash Point Determination (°C)
B.napus	86.99±5.15	7.62±4.17	249±10.50	4.98±0.70	195±3
S.arvensis-1	91.56±0.58	11.49±0.30	262±2.50	6.08±0.40	194±2
S.arvensis-2	90.59±1.55	11.47±0.32	306±46.50	5.93±0.25	193±1
B.nigra-1	93.52±1.38	12.86±1.07	231±28.50	5.77±0.09	192±0
B.nigra-2	95.99±3.85	13.61±1.82	267±7.50	5.51±0.17	188±4
B.nigra-3	94.19±1.99	13.70±1.91	242±17.50	5.79±0.11	190±2

CONCLUSION

Crowded world population and developing industrialization increase environmental pollution. In addition, the depletion of fossil fuels, reveals the search for alternative fuel sources. Thus, biofuels of vegetable origin are becoming interesting. In the light of all this information, the adaptation of vegetable-based fuels to growing conditions is economically important. Wild plants should be primarily evaluated in order to determine the usability of plants with high adaptability to different environmental conditions, high yield values, and resistant to diseases and pests in biofuel production.

Fatty acid composition and biodiesel quality analysis results of *Sinapis arvensis* and *Brassica nigra* were not same with *B.napus*, but close results were obtained. Lipid yield of wild local breeds were quite high and it’s so important for bioenergy production. The results obtained in this study show that; wild *S.arvensis* and *B.nigra* local breeds have a big potential to become crude materials in biodiesel production. Although *S.arvensis* and *B.nigra* are still wild plants, it has been determined that plants have similar properties in oil yield, fatty acid composition and biodiesel quality characteristics with *B.napus*. When all these similarities and the economic importance of biodiesel are evaluated; it is considered important to cultivate wild *S.arvensis* and *B.nigra* local breeds as alternative energy plants. By making more comprehensive analogues of this study, it will be possible to obtain more data about these plants with economic value.

ACKNOWLEDGMENTS

This study was supported by Bayburt University Scientific Research Projects Unit with the project numbered 2017/02-69001-20.

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