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Araştırma Makalesi

Ham, Rafine ve Kızartılmış Aspir Yağlarından Üretilen Biyodizellerin Yakıt Özelliklerinin İncelenmesi

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ÖZ

Bu çalışmada, aspir (*Carthamus tinctorius* L.) ham ve rafine yağlarından üretilen biyodizellerin ve bu yağların kızartmada kullanımı sonucu elde kalan atık aspir ham yağı ile atık aspir rafine yağlarından üretilen biyodizellerin yakıt analizleri yapılmıştır. Aspir; ham yağdan, rafine yağdan, atık ham yağdan ve rafine atık yağlardan üretilen biyodizellerin sırasıyla; 15°C deki yoğunluğu (883.2)-(896.3)-(889.8)-(877.9) kg m^{-3}, 40°C deki kinematik viskozitesi (4.57)-(5.55)-(5.72)-(4.86) mm^2s^{-1}, soğuk filtre tıkanma noktası (SFTN) (-8), (-9), (-12), (-11) °C, ısıl değeri (39.857)-(39.137)-(39.095)-(39.508) MJ kg^{-1}, parlama noktası (160)-(150)-(180)-(180)°C, su içeriği (398)-(386)-(206)-(243) mg kg^{-1}, renk (ASTM D1500) (<0.5)-(<0.5)-(<0.5)-(1.2), bakır şerit korozyon bütün yakıtlarda (1a) olarak tespit edilmiştir. Elde edilen sonuçlara göre; aspir ham yağı, rafine yağı ve bunların atık kızartma yağlarından yapılan biyodizellerin EN 14214 standardına göre sadece rafine aspir yağı biyodizeli ve atık ham aspir yağı biyodizellerinin kinematik viskozite değerlerinin yüksek çıktığı, diğer yapılan analizlerde standartlar içinde olduğu görülmüştür.

Anahtar kelimeler: Aspir yağı, atık yağ, biyodizel, yakıt özellikleri

Investigation of Fuel Properties of Biodiesel Produced from Crude, Refined and Fried Safflower Oils

ABSTRACT

This study examined the fuel properties of biodiesels derived from safflower (*Carthamus tinctorius L.*) crude and refined oils, as well as those produced from waste safflower crude oil and waste safflower refined oil generated from frying. Biodiesel produced from safflower crude oil, refined oil, waste crude oil and waste refined oil, respectively; Density at 15°C (883.2)-(896.3)-(889.8)-(877.9) kg m^{-3}, kinematic viscosity at 40°C (4.57)-(5.55)-(5.72)-(4.86) mm^2s^{-1} cold filter plugging point (SFTN) (-8), (-9), (-12), (-11) °C, calorific value ((39.857)-(39.137)-(39.095)-(39.508) MJ kg^{-1}, flash point (160)-(150)-(180)-(180)°C, water content (398)-(386)-(206)-(243) mg kg^{-1}, colour (ASTM D1500) (<0.5)-(<0.5)-(<0.5)-(1.2), copper strip corrosion were determined as (1a) in all fuels. revealing that only the kinematic viscosity values of refined safflower oil biodiesel and waste crude safflower oil biodiesel exceeded the standard specified in EN 14214 for biodiesels derived from safflower crude oil, refined oil, and their waste frying oils, while the other fuel properties were found to be within the established standards.

Key words: Biodiesel, fuel properties, safflower oil, waste oil

INTRODUCTION

Safflower (*Carthamus tinctorius L.*) is an annual plant belonging to the *Compositae (Asteraceae*) family and is categorized as an oilseed crop. It can be cultivated in both winter and summer seasons (Eryılmaz et al., 2014; Arslan and Güler, 2022). Safflower typically grows to a height of 85-110 cm and exists in thorny and thornless forms. It bears flowers in a variety of colors, including yellow, white, cream, red, and orange, and its seeds are found in white, brown, and white grains with dark lines. The plant branches out and produces small trays of seeds at the end of each branch. Its colored flowers (petals) are used for food and fabric dyeing. Safflower has a taproot system that can extend up to 3 m deep. Its seeds contain approximately 30-50% oil, 15-20% protein, and 35-40% husk. Safflower is an annual, long-day oil plant that comprises two different types, namely Linoleic (Omega-6) and Oleic (Omega-9, with similar quality to olive oil). Its oil is of high quality and can be used for various purposes such as edible consumption, biodiesel production, medicine, cosmetic industry, and ornamental plants. Additionally, its meal can be used as animal feed. It is drought-resistant and can grow between 110-140 days on average during the summer season (Sefaoğlu, 2022). The unique characteristic of safflower oil is its high unsaturated fatty acid content and low saturated fatty acid content. Its primary unsaturated fatty acids are oleic and linoleic acids. Among vegetable oil varieties, safflower oil has the lowest total saturated fatty acid level (Baran and Andırma, 2019). Due to its ecological characteristics, Turkey possesses a vast production potential for cultivating numerous oil crops. Safflower, which is one of Turkey's indigenous plants and is found in many wild species in Anatolia, exhibits higher resistance to drought, heat, and soil salinity than other oil crops such as soya, rapeseed, sunflower, and peanut originating from other continents. As a result, the cultivation of safflower has gained significant importance both globally and within Turkey, particularly in response to the drought brought about by global warming and the search for alternative crops suitable for such conditions (Baydar and Erbaş, 2020). Safflower, a hardy oilseed crop capable of thriving in barren environments, has emerged as a promising resource for Turkey's vegetable oil and compound feed sectors. Its potential is derived from its ability to be cultivated in non-traditional regions, rotated with other crops, and grown on fallow land without posing a significant risk to cereal production or jeopardizing food security (İlkdoğan, 2012). Thus, safflower represents a valuable opportunity for sustainable and diversified agricultural production in Turkey.Based on data from the Food and Agriculture Organization (FAO) in 2021, the cultivation of safflower occupies approximately 850 431 hectares of land globally, resulting in a production of 631 051 tonnes of safflower seeds. The mean yield of safflower worldwide is estimated to be approximately 74.2 kg da^{-1}. Safflower production is distributed across various regions of the world, with 52.7% of it occurring in Asia, 24% in Europe, 19% in America, 3.7% in Africa, and 0.6% in Oceania. Among the countries producing safflower, Kazakhstan ranks first, with a production of 223 895 tonnes, followed by Russia, the United States, Mexico, India, China, Turkey, Tanzania, Ethiopia, and Tajikistan. Turkey ranks seventh globally in terms of safflower production, following China (Anonymous, 2023a). In recent years, the cultivation of safflower has experienced a significant increase in Turkey, especially in dry agricultural areas where fallow practices are employed. The cultivation area of safflower has significantly expanded from 300 decares in 2000 to 262 375 decares in 2022, resulting in an increase in production from 18 tonnes to 30 000 tonnes and seed yield from 60 kg ha^{-1} to 114 kg ha^{-1} (Anonymous, 2023h). This progress can be attributed, in part, to the agricultural subsidies provided by the government, which have been instrumental in supporting the cultivation of oilseed crops, including safflower. It is critical to conduct research and development studies to further enhance the role of Turkey in global safflower production and to bolster the contribution of safflower to the domestic agricultural and economic landscape. Table 1 presents the cultivated area, production, and yield values of oilseed crops grown in Turkey. Table 2 provides information on the characteristics of registered safflower varieties in the country. Although Turkey has a high potential for oil and oilseed enterprises, it is worth noting that limited research has been conducted on alternative oilseed crops and their fuel-related properties. Thus, this study aims to investigate the fuel properties of crude and refined safflower (*Carthamus tinctorius L.)* oil, as well as the biodiesel produced from these oils, along with the biodiesel obtained from waste frying oils.

Table 1. Cultivated area, production and yield values of oilseed crops in Turkey by years (Anonymous, 2023a)

Oilseed Plants		2018	2019	2020	2021	2022
Soy	Area harvested (da)	328.483	352.947	351.343	438.917	380.090
	Production (Tonnes)	140.000	150.000	155.225	182.000	155.000
	Yield (kg da^{-1})	426	425	442	415	408
Peanut	Area harvested (da)	443.342	424.211	547.747	579.192	457.016
	Production (Tonnes)	173.835	169.328	215.927	234.167	186.340
	Yield (kg da^{-1})	392	399	394	404	408
Sunflower (Oil)	Area harvested (da)	6.489.344	6.759.834	6.508.696	8.113.116	9.005.177
	Production (Tonnes)	1.800.000	1.950.000	1.900.000	2.215.000	2.350.000
	Yield (kg da^{-1})	277	288	292	273	261
Sesame	Area harvested (da)	259.858	248.604	256.663	254.862	242.857
	Production (Tonnes)	17.437	16.893	18.648	17.657	17.366
	Yield (kg da^{-1})	67	68	73	69	72
Safflower	Area harvested (da)	246.932	158.601	151.150	145.882	262.375
	Production (Tonnes)	35.000	21.883	21.325	16.200	30.000
	Yield (kg da^{-1})	142	138	141	111	114
Rape	Area harvested (da)	378.456	525.146	349.981	376.017	411.455
	Production (Tonnes)	125.000	180.000	121.542	140.000	150.000
	Yield (kg da^{-1})	330	343	347	372	365
Cotton Seed	Area harvested (da)	-	-	-	-	-
	Production (Tonnes)	1.542.000	1.320.000	1.064.189	1.350.000	1.650.000
	Yield (kg da^{-1})	297	276	296	312	288
Linseed	Area harvested (da)	0	0	0	10	95
	Production (Tonnes)	0	0	0	0,5	8
	Yield (kg da^{-1})	-	-	-	50	84
Hemp	Area harvested (da)	59	536	4.252	317	1.963
	Production (Tonnes)	3	20	273	20	159
	Yield (kg da^{-1})	51	37	64	63	81
Poppy	Area harvested (da)	-	-	-	-	-
	Production (Tonnes)	26.991	27.288	20.542	21.037	12.240
	Yield (kg da^{-1})	60	40	45	41	30

Table 2. Some characteristics of registered safflower cultivars grown in Turkey (Anonymous, 2023b; Anonymous, 2023c; Anonymous, 2023d; Anonymous, 2023e; Anonymous, 2023f; Anonymous, 2023g; Anonymous, 2023k; Arslan et al., 2019; Baydar and Erbaş, 2020; Eryılmaz and Ark., 2014; Koç , 2019; Öğüt et al., 2012)

Variety Name	Spiny/ Spineless	Flower colour	Plant Height (cm)	Seed colour	Oil content (%)	1000 seed weight (g)	Date of registration
Yenice 5-38	Spineless	Red	100-120	White	24-25	38-40	16.05.1964
Dinçer (5-18-1)	Spineless	Orange	90-110	White	25-28	45-49	06.05.1983
Remzibey 05	Spiny	Yellow	60-80	White	35-40	46-50	26.04.2005
Balcı	Spiny	Yellow	55-70	Cream	38-41	40-48	06.04.2011
Linas	Spiny	Orange	85-90	Cream	37-38	40-44	10.04.2013
Olas	Spiny	Yellow	90-100	Cream	39-41	38-42	31.03.2015
Göktürk	Spiny	Orange	90-100	White	34-35	40-45	13.04.2016
Asol	Spiny	Orange	70-80	White	40-41	45-48	11.04.2018
Hasankendi	Spiny	Yellow	80-90	White	35-36	38-45	11.04.2018
Olein	Spiny	Red	70-90	White	31-36	34-44	08.04.2019
Askon42	Spiny	Orange	70-90	White	33-37	36-54	08.04.2019
Yekta	Spiny	Yellow	80-100	White	35-37	40-50	08.04.2019
Servetağa	Spiny	Yellow	85-90	White	35-40	35-40	08.04.2019
Koç42	Spiny	Yellow	70-90	Cream	37-39	40-50	08.04.2019
Safir	Spiny	Orange	70-150	White	33-39	40-42	08.04.2019

MATERIALS AND METHODS

The present study outlines the procedures undertaken to produce biodiesel from safflower crude oil and refined safflower oil. The transesterification method was employed in a two-stage process, utilizing a magnetic stirrer with heater at the Biofuel Laboratory of the Department of Agricultural Machinery and Technologies Engineering, Faculty of Agriculture, Selçuk University. The devices and laboratory used in fuel analysis are given in Figure 1. These measurements were made according to the device and working methods given in Table 3.

Figure 1. The devices and laboratory used in fuel analysis
a)Laboratory b) Density c) Kinematic viscosity d) Flash point e) Water content f) Calorific value g) Freezing point h) Copper strip corrosion i) Cold Filter Plugging Point j) Colour

To produce 2 litres of biodiesel, the first reaction involved the use of 400 mL of methyl alcohol and 7 g of sodium hydroxide. Specifically, 75% methanol (Merck, d=0.791-0.792 kg/l) and 50% NaOH (Merck) catalyst, comprising 300 mL of methyl alcohol and 3.5 g NaOH were dissolved in the magnetic stirrer to obtain methoxide. This methoxide was added to the oil and stirred at 55°C with a stirrer speed of 1000 min^{-1} for 90 minutes. Following this, the mixer and heater were stopped, and the glycerol was allowed to precipitate for 120 minutes and subsequently removed. Thereafter, the second stage was initiated. In the second reaction, a mixture of methyl alcohol (25%, 100 ml) and NaOH (50%, 3.5 g) was prepared via magnetic stirring to obtain methoxide. The first reaction involving the crude biodiesel was subsequently reheated to 55°C by activating the mixer, and methoxide was then added to the mixture and allowed to react for 60 minutes. Following this, the mixer and heater were deactivated, and the reaction mixture was allowed to rest for 120 minutes to facilitate the separation of glycerol. The resulting glycerol was collected, and the temperature of the crude biodiesel was subsequently increased to 75°C to facilitate the removal of methyl alcohol. The glycerol was then allowed to precipitate for 12 hours, following which it was separated from the reaction mixture. Subsequently, the pH value of the biodiesel was measured and, as the reaction was found to be basic, the biodiesel underwent washing through the mist method employing distilled water until neutralization was achieved. The primary objective of this washing step was to eliminate any unreacted alcohol, residual fatty acids, Na+, K+ ions, catalysing agents, and glycerol that may have been retained in the biodiesel during separation. The washing procedure was conducted at a temperature of 50°C, employing a total of 200 millilitres of pure water that was also maintained at 50°C. Following the washing procedure, the water-biodiesel mixture was allowed to settle for a duration of 12 hours. Subsequently, the precipitated water was separated from the biodiesel using a separation funnel. The washed biodiesel was subjected to a drying process at a temperature of 120°C, which exceeds the boiling point of water, and this process was maintained for a duration of 2 hours. Consequently, the production of biodiesel from safflower crude oil was achieved. Several fuel analyses were subsequently performed on the resulting biodiesel at the Biofuel Laboratory of Selçuk University, Faculty of Agriculture, Department of Agricultural Machinery and Technologies Engineering. The analysis results of various samples, including crude safflower oil (CSO), refined safflower oil (RSO), crude safflower oil biodiesel (CSOB), refined safflower oil biodiesel (RSOB), waste crude safflower oil biodiesel (WCSOB), and waste refined safflower oil biodiesel (WRSOB), are presented in Table 3.

Table 3. Specifications of Test Devices

Fuel Characteristic	Devices	Measurable range	Unit	Measuring accuracy	Manufacturer	Standard
Density	Kem Kyoto DA-130N	0.0000 - 2.0000	g cm^{-3}	±0.0001	Kem Kyoto Elektronik, Japonya	EN ISO 3675 EN ISO 12185
Kinematic viscosity at 40°C	Koehler K23377	Ambient temperature – 150	mm^2 s^{-1}	±0.01	Koehler Instrument Company, US	EN ISO 3104
Flash point	Koehler K16270	Ambient temperature - 370	°C	±0.01	Koehler Instrument Company, USA	EN ISO 2719 EN ISO 3679
Water content	Kem Kyoto MKC-501	10µg-100mg	µg	±0.01	Kem Kyoto Elektronik, Japonya	EN ISO 12937
Calorific value	IKA C 200	0-40.000	J	±0.0001	IKA, UK	DIN 51900
Cold Filter Plugging Point	Tanaka AFP-102	-60 °C	°C	±0.01	Tanaka Scıentıfıc Lımıted, Japonya	ASTM D6379
Freezing point	Koehler K46000	(-80)… (+20)	°C	±0.01	Koehler Instrument Company, USA	ASTM D97 ASTM D2500
Copper strip corrosion	Koehler K 25330	0-190		±0.01	Koehler Instrument Company, USA	EN ISO 2160
Colour	Lovibond PFX195	0.5 – 8	unit	±0.0004	Lovibond, Germany	ASTM D1500

RESULTS AND DISCUSSION

Safflower is a valuable oil plant whose significance is rapidly increasing worldwide due to its high adaptability to arid regions, as well as its cold and salinity tolerance (Baydar and Turgut, 1993; Kayaçetin et al., 2012). Unlike other oilseed crops, safflower can be sown both in winter and summer seasons, with winter sowing typically resulting in a higher oil yield. Additionally, safflower seeds can be processed into oil without requiring the use of any separate or additional machinery, nor necessitating any modifications to sunflower processing facilities. Including alternative oil crops such as safflower in the crop pattern is crucial in addressing the oil deficit of various countries. According to the results in Table 4, some fuel analyses of biodiesels produced from safflower (Carthamus tinctorius L.) crude oil and refined oil and biodiesels produced from waste safflower crude oil and waste safflower refined oil as a result of the use of these oils in frying were carried out. Biodiesel produced from safflower crude oil, refined oil, waste crude oil and waste refined oil, respectively; Density at 15°C (883.2)-(896.3)-(889.8)-(877.9) kg m^{-3}, kinematic viscosity at 40°C (4.57)-(5.55)-(5.72)-(4.86) mm^2 s^{-1}, cold filter plugging point (SFTN) (-8), (-9), (-12), (-11) °C, calorific value (39.857)-(39.137)-(39.095)-(39.508) MJ kg^{-1}, flash point (160)-(150)-(180)-(180) °C, water content (398)-(386)-(206)-(243) mg kg^{-1}, color (ASTM D1500) (<0.5)-(<0.5)-(<0.5)-(1.2), copper strip corrosion were determined as (1a) in all fuels. In addition, these results are given in Figure 2. According to the results obtained; according to EN 14214 standard of biodiesels produced from safflower crude oil, refined oil and their waste frying oils, only the kinematic viscosity values of refined safflower oil biodiesel (5.55 mm^2 s^{-1} (at 40°C)) and waste crude safflower oil biodiesel (5.72mm^2 s^{-1} (at 40°C)) were found to be high, and the other analyses were within the limit values of EN 14214 standard.

Table 4. Fuel properties of safflower (*Carthamus tinctorius L.*) crude oil, refined oil and biodiesel produced from these oils and biodiesel obtained from waste frying oils of these oils.

Fuel Characteristics	**CSO**	**RSO**	**CSOB**	**RSOB**	**WCSOB**	**WRSOB**	**EN 14214**	
							Min.	**Maks.**
Density, kg m^{-3}, (15°C)	916.3	920.7	883.2	896.3	877.9	889.8	860	900
Kinematic viscosity, mm^2 s^{-1}, (40°C)	29.9	31.8	4.57	5.55	4.86	5.72	3.5	5.0
Cold filter plugging point, °C	-	-	-8	-9	-11	-12		
Calorific Values, MJ kg^{-1}	39.025	37.478	39.857	39.137	39.508	39.095		
Flash Point, °C	-	-	160	150	180	180	120	
Water content, mg kg^{-1}	394	378	398	386	243	206		500
Colour	1.9	0.5	<0.5	<0.5	1.2	<0.5	-	-
Copper Strip Corrossion, (3h 50°C)	1a	1a	1a	1a	1a	1a	1	
Freezing point, °C	-17	-18	<-20	<-20	<-20	<-20	-	-

In a study conducted by Işık (2016), the density of refined safflower biodiesel was reported to be 891 kg m^{-3}, which was found to be higher compared to that of canola biodiesel. Similarly, Almedia (2014) reported that the kinematic viscosity value of biodiesel derived from waste frying oil was found to be higher according to EN 14214 standard. This may be attributed to the partial hydrogenation of waste frying oil, resulting in a higher proportion of trans fatty acid chains (Knothe, 2005). Falizi (2019) investigated the effects of different irrigation schedules on the production of refined safflower oil from safflower seeds and reported that the viscosity value of biodiesel produced from these refined oils varied between 4.81-5.77 mm^2 s^{-1}, depending on the irrigation schedule. There are many factors that contribute to high viscosity values, including the irrigation plan.

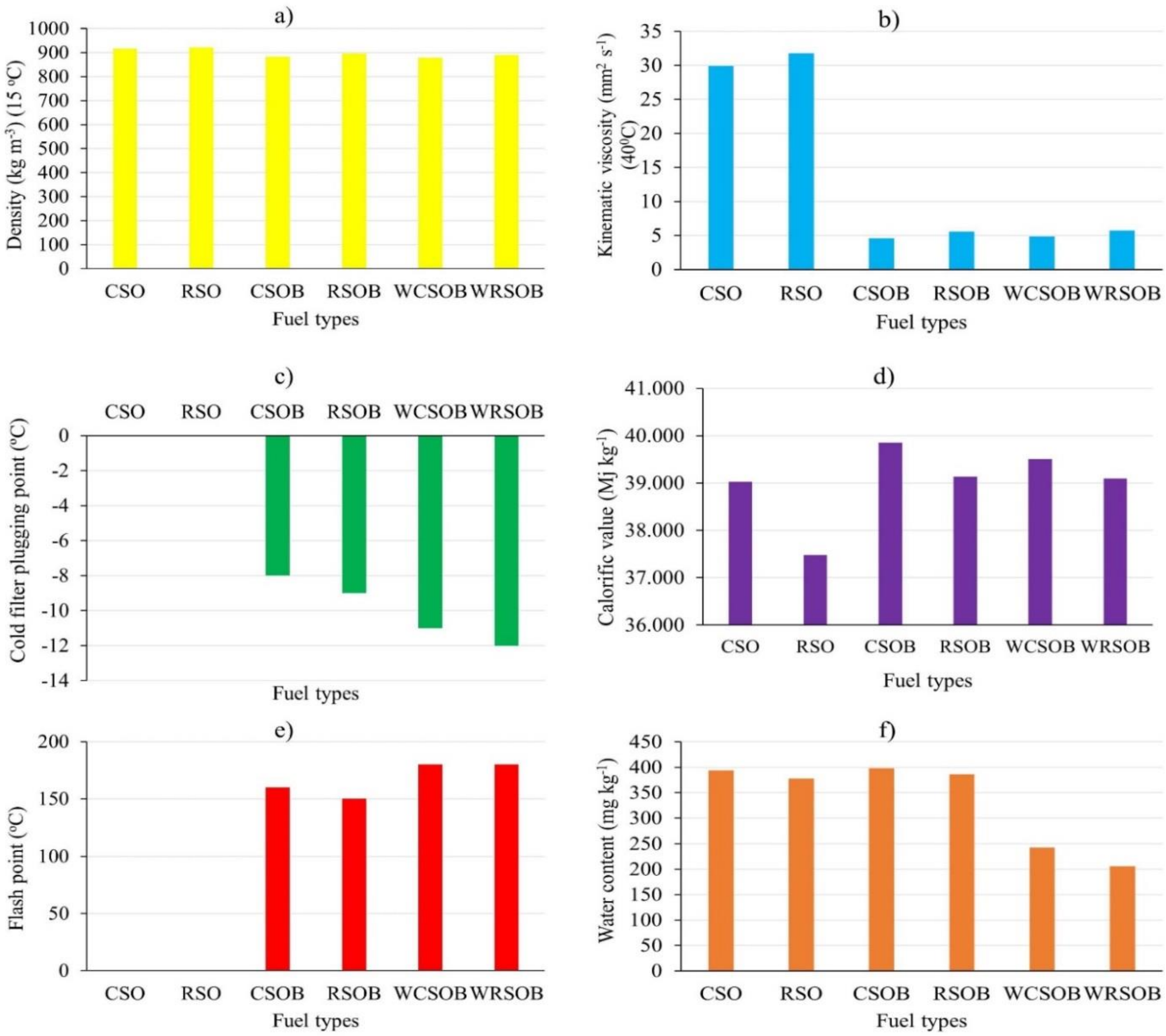

Figure 2. Graphical view of results

CONCLUSIONS

The viscosity values of both refined safflower oil biodiesel and waste crude safflower oil biodiesel, which were produced from crude and refined safflower oil (Carthamus tinctorius L.), failed to meet the requirements outlined in the EN 14214 standard. Specifically, the viscosity values for refined safflower oil biodiesel and waste crude safflower oil biodiesel exceeded the maximum limit outlined in EN 14214 by 9.9% and 12.5%, respectively. To bring the viscosity values of these biodiesels within appropriate standards, the use of high alcohols such as butanol can be employed. It is recommended that engine performance and exhaust emission tests be conducted on these fuels following the appropriate modifications to evaluate their efficacy.

Çıkar Çatışması Beyanı: Makale yazarları aralarında herhangi bir çıkar çatışması olmadığını beyan ederler.

Araştırmacıların Katkı Oranı Beyan Özeti: Yazarlar makaleye eşit oranda katkı sağlamış olduklarını beyan ederler.

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