

Determination of Some Physicochemical Properties of Binary Biodiesel and Binary Biodiesel-Diesel Blend Fuels Obtained from Waste Pumpkin Seed- Camelina Oils

Seda ŞAHİN^{1*} 

¹Selçuk University, Faculty of Agriculture, Department of Agricultural Machinery and Technology Engineering, Konya

*Sorumlu Yazar: sedabacak@selcuk.edu.tr

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ABSTRACT

The primary aim of utilizing biodiesel is reduce dependency on fossil fuels, decrease harmful emissions, and promote the use of renewable energy sources. Studies on biodiesel commonly revolve around singular biodiesel-petroleum diesel blends. The combination of these diverse feedstocks with distinct properties can offer varying characteristics and benefits. Many studies regarding liquid biofuels primarily focus on blends of singular biodiesel with diesel. Raw materials constitute a substantial portion of the cost in biodiesel production. Hence, efforts have been made to favor non-edible and waste products as raw materials. Additionally, products that are suitable for cultivation in Turkey and easy to obtain as raw materials, supporting domestic biofuel production, have been chosen. Biodiesels obtained from waste pumpkin seeds and camelina oils through the transesterification method were blended at volumetric ratios of 1:1 and 1:3 to obtain binary biodiesel fuels (C50P50, C25P75, and C75P25). The binary biodiesel-diesel blend fuels were achieved by blending different volume ratios of binary biodiesel fuels (C25P25D50 and C10P10D80) with traditional petroleum diesel after their preparation. Subsequent analyses focused on determining the physicochemical properties (density, kinematic viscosity, flash point, water content, calorific value, cold filter plugging point, and copper strip corrosion) of the prepared binary biodiesel and binary biodiesel-diesel blend fuels. Compliance with biodiesel standards (EN 14214, ASTM D-6751) was observed for all fuels, and the results were compared with the reference fuel, diesel (petroleum). According to the analysis results, all the tested fuels met the standards, with the C10P10D80 blend fuel displaying the closest resemblance to diesel.

Key words: Waste pumpkin oil, Camelina oil, Binary biodiesel, Fuel properties.

Atık Kabak Çekirdeği - Ketencik Yağlarından Elde Edilen İkil Biyodizel ve İkil Biyodizel – Dizel Karışım Yakıtlarının Bazı Fizikokimyasal Özelliklerinin Belirlenmesi

ÖZ

Biyodizel kullanmanın temel amacı fosil yakıtlara olan bağımlılığı azaltmak, zararlı emisyonları azaltmak ve yenilenebilir enerji kaynaklarının kullanımını teşvik etmektir. Biyodizel üzerine yapılan çalışmalar genellikle tekil biyodizel-petrol dizel karışımları etrafında dönüyor. İkil biyodizel genellikle farklı türdeki biyodizellerin karıştırılması veya bu karışımların petrol dizeli ile harmanlanmasıyla elde edilir. Bu farklı hammaddelerin farklı özelliklere sahip kombinasyonu, farklı özellikler ve faydalar sunabilir. Sıvı biyoyakıtlarla ilgili birçok çalışma öncelikle tekil biyodizelin dizel ile karışımlarına odaklanmaktadır. Biyodizel üretiminde maliyetin önemli bir kısmını hammaddeler oluşturmaktadır. Bu nedenle yenmeyen ve atık ürünlerin hammadde olarak tercih edilmesine yönelik çalışmalar yapılmıştır. Ayrıca Türkiye'de ekime uygun, hammadde olarak temini kolay, yerli biyoyakıt üretimini destekleyen ürünler tercih edilmiştir. Atık kabak çekirdeği ve keten tohumu yağlarından transesterifikasyon yöntemiyle elde edilen biyodizeller, hacimsel olarak 1:1 ve 1:3 oranlarında harmanlanarak ikil biyodizel yakıtlar (C50P50, C25P75 ve C75P25) elde edildi. İkil biyodizel-dizel karışımı yakıtlar, farklı hacim

oranlarındaki ikili biyodizel yakıtların (C25P25D50 ve C10P10D80) geleneksel petrol dizeli ile hazırlandıktan sonra harmanlanmasıyla elde edilmiştir. Daha sonraki analizler, hazırlanan ikili biyodizel ve ikili biyodizel-dizel karışımı yakıtların fizikokimyasal özelliklerinin (yoğunluk, kinematik viskozite, parlama noktası, su içeriği, kalorifik değer, soğuk filtre tıkanma noktası ve bakır şerit korozyonu) belirlenmesini kapsamaktadır. Tüm yakıtlarda biyodizel standartlarına (EN 14214, ASTM D-6751) uygunluk gözlemlenmiş ve sonuçlar referans yakıt olan dizel (petrol) ile karşılaştırılmıştır. Analiz sonuçlarına göre, test edilen yakıtların tamamı standartlara uygun olup, dizele en yakın benzerliği C10P10D80 karışım yakıtı göstermiştir.

Anahtar kelimeler: Atık kabak yağı, Ketencik yağı, İkili biyodizel, Yakıt özellikleri

INTRODUCTION

Derived from organic sources like vegetable oils, animal fats, or recycled cooking greases, biodiesel stands as a sustainable and cleaner alternative to traditional diesel fuel, widely applicable in transportation and diverse industrial sectors. A major advantage of biodiesel lies in its significant environmental impact. In comparison to petroleum-based diesel, biodiesel notably diminishes greenhouse gas emissions, including carbon dioxide, sulfur dioxide, and particulate matter, crucial contributors to air pollution and global warming. Its integration in diesel engines leads to reduced levels of harmful emissions, potentially mitigating the environmental footprint associated with transportation and various industries. Ongoing research and development consistently explore advanced technologies, alternative feedstocks, and more efficient production methods to bolster the viability and scalability of biodiesel as a mainstream fuel option.

The blending of biodiesels obtained from different sources offers the potential to create a product with optimized properties that are not inherent in individual feedstocks. Through binary biodiesel blending, the balancing of raw material supply and cost becomes feasible. The amalgamation of diverse biodiesels enables a more stable and cost-effective production process. Fuels resulting from blending various biodiesels may possess superior combustion properties, thereby proving more effective in reducing emissions.

This approach could potentially offer advantages in diversifying biodiesel sources, improving performance, and rendering the production process more adaptable and cost-effective. However, the specific composition and effects of such blends can significantly vary based on the combination of raw materials used and the blending ratios applied.

In a study by Gupta and Sharma (2023), the fuel properties, engine performance, and emissions of binary mixtures of *Jatropha curcas* biodiesel and waste cooking oil (WCO) were analyzed. They found that the 80% WCO biodiesel and 20% *J. curcas* biodiesel blend exhibited the most suitable fuel properties when tested in a diesel engine compared to diesel fuel. For this binary mixture, they observed a substantial decrease in engine emissions of carbon monoxide and unburned hydrocarbons but noted increased carbon dioxide and nitrogen oxide (NO_x) emissions in comparison to diesel. At full load, they determined the BSFC to be 396.82 g/kWh (15.76% higher than diesel) and the BTE to be 22.7% lower than diesel.

Singh et al. (2020) investigated the impact of a blend consisting of 70% amla seed oil biodiesel and 30% eucalyptus oil (AB70EU30) on engine and emission parameters. Through adjustments to the engine's compression ratio, injection timing, and pressure, they observed that the use of AB70EU30 fuel in a modified engine led to increased Brake Thermal Efficiency (BTE) and decreased Brake Specific Fuel Consumption (BSFC) in comparison to conventional diesel fuel. Additionally, they noted enhanced combustion, resulting in reduced emissions.

Nita et al. (2011), explored the utilization of a dual blend comprising poppy and waste cooking (PWC) biodiesel-diesel blends in a CI engine. Through experiments, they mixed PWC fuel with diesel at varying ratios of 5%, 10%, and 20% under different engine loads. Their investigation unveiled a significant decline in carbon monoxide (CO), hydrocarbon (HC), and particulate matter (PM) emissions during full load conditions compared to conventional diesel usage. Nevertheless, an uptick in NO_x emissions was noted.

Da Ponte et al. (2015) study aimed to produce second-generation biodiesel by blending castor oil with cotton, rapeseed, and soybean oils. They generated binary mixtures of plant oils at varying mass ratios through alkali transesterification using methanol and ethanol. Results indicated that binary mixtures of plant oils might serve as an alternative with reduced use of edible raw materials for biodiesel production. In another study by Nayak et al. (2021), the performance of a binary mixture of fish oil and WCB was tested, revealing superior quality fuel with reduced smoke, CO, and HC emissions.

Habibullah et al. (2015) conducted a study evaluating the performance and emissions of a single-cylinder diesel engine using blends of palm or coconut biodiesel and their combinations. They found that a fixed final blend of combined palm-coconut biodiesel reduced NO_x emissions by 0.54% to 1.85%, slightly

enhancing brake power and Brake Specific Fuel Consumption (BSFC). This blend combined the advantages of coconut's high cetane number and palm's excellent ignition quality.

In our research, biodiesel derived from two different types of oils was produced to ensure diversity in raw materials. Fuels obtained from mixtures of camelina and waste pumpkin seed oils were blended with diesel fuel in various ratios, creating binary biodiesel-diesel mixtures and binary biodiesel blends at volumetric ratios of 1:1 and 1:3 among themselves. The study aimed to determine the physicochemical properties of these binary biodiesels and binary biodiesel-diesel fuels, assessing their compliance with relevant biodiesel standards (EN 14214, ASTM D-6751).

MATERIAL and METHODS

The waste pumpkin seed used for biodiesel production in the research was obtained from Çumra Pumpkin Producers Association (Figure 1). Camelina seeds used to produce Camelina biodiesel were of Arslanbey variety and obtained from the Central Research Institute of Field Crops of the Ministry of Agriculture and Forestry (Figure 2). The oil extraction process from camelina and waste pumpkin seeds was carried out in 3 stages. The seeds were first crushed in a crushing machine for pre-treatment, heated and annealed, and then cold pressed in a 200 ton hydraulic press to separate the oil from the oil meal. Petrodiesel, which will be used as a reference for comparison in blend fuels, was obtained from the market.



Figure 1. Waste pumpkin seeds



Figure 2. Camelina seed (Arslanbey variety)

Filtering of waste pumpkin seed and camelina oils

The waste pumpkin seed and camelina (Arslanbey variety) oils obtained by hydraulic pressing were firstly passed through filter paper and filtration process was applied. The conditions of the oils before and after the filtering process and the filtration process applied to the oils are shown in Figure 3.



Figure 3. Filtration process applied to waste pumpkin seed and camelina oils

Stages of biodiesel production from waste pumpkin seed and camelina oils

After filtration of both oils, transesterification method was used for the production of waste pumpkin seed biodiesel (P100) and camelina biodiesel (C100). Methyl alcohol was used to decompose glycerol components in oils and sodium hydroxide (NaOH) was used as a catalyst to decompose triglyceride in biodiesel production from oils consisting of different raw materials (Şahin, 2021).

Methyl alcohol (CH₃OH) was used at the rate of 20% of the filtered crude oil and 3.5 g of sodium hydroxide (NaOH) per 1 liter as catalyst. Methyl alcohol and sodium hydroxide were stirred until dissolution and methoxide was obtained. The methoxide was mixed with crude oil at 55 °C, the reaction temperature of which was kept constant in a thermostat controlled heater with magnetic stirrer. The reaction temperature was kept constant for 1 hour and the mixing process continued for 8 hours for the separation of methyl ester and glycerol in the oil and glycerin was separated from methyl ester. The temperature of the methyl ester separated from glycerin was raised to 75°C and the remaining methyl alcohol (CH₃OH) was removed. Washing was performed for reasons such as removal of unreacted alcohol, fatty acids, catalyst material and remaining glycerol during esterification. The washing process was carried out using distilled water at 20% of the methyl ester and the used water and unreacted substances were allowed to settle and the waste water was separated from the crude biodiesel. The biodiesel was dried by stirring in a magnetic stirrer at a temperature of 100°C to remove the water. (Balci, 2017; Eryilmaz et al., 2022; Şahin, 2021)

The production steps described in the transesterification process were applied for both oils and C100 and P100 biodiesels were produced. The change of oils in the production stages described above is given in Figure 4.

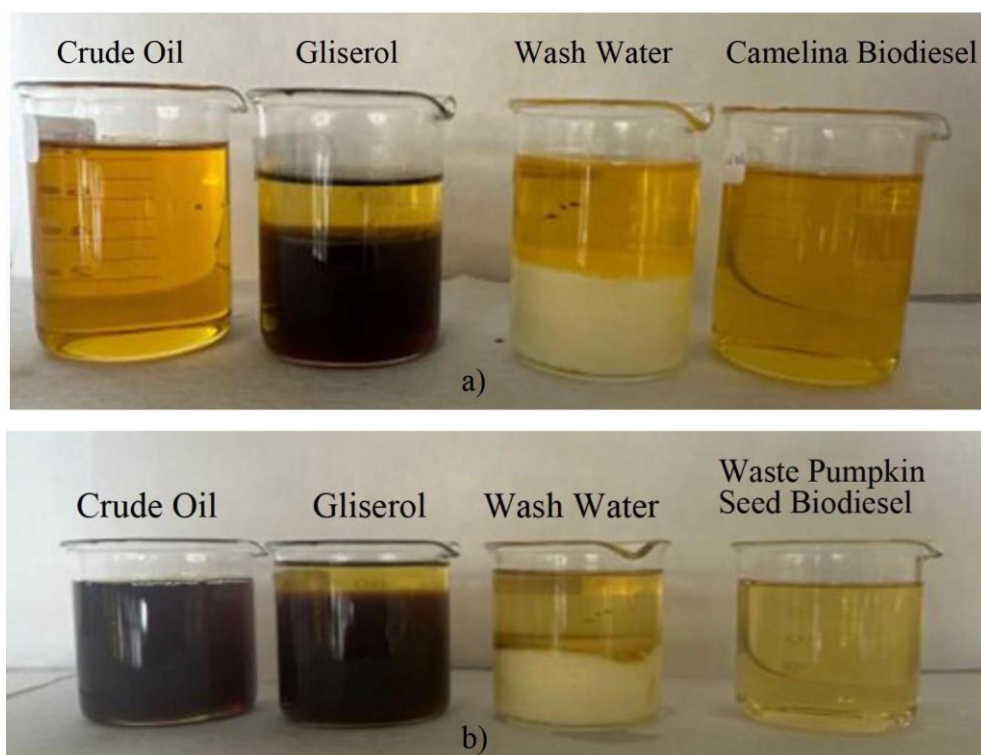


Figure 4. Production stages of camelina biodiesel (a) and Waste pumpkin seed biodiesel (b) produced by transesterification method

Preparation of blend fuels

The % mixture ratios of the fuels and blends prepared for the determination of fuel properties and the general appearances of these fuels are shown in Table 1 and Figure 5, respectively. For ease of use, diesel is symbolised as "D", camelina biodiesel as "C" and waste pumpkin seed biodiesel as "P". The numbers added as indices under the symbols represent the blend ratios of the fuels.

Table 1. Prepared fuels and % mixture ratios

Fuels	P (%)	C (%)	D (%)
D100	-	-	100
P100	100	-	-
C100	-	100	-
P50C50	50	50	-
P25C75	25	75	-
P75C25	75	25	-
D50P25C25	25	25	50
D80P10C10	10	10	80

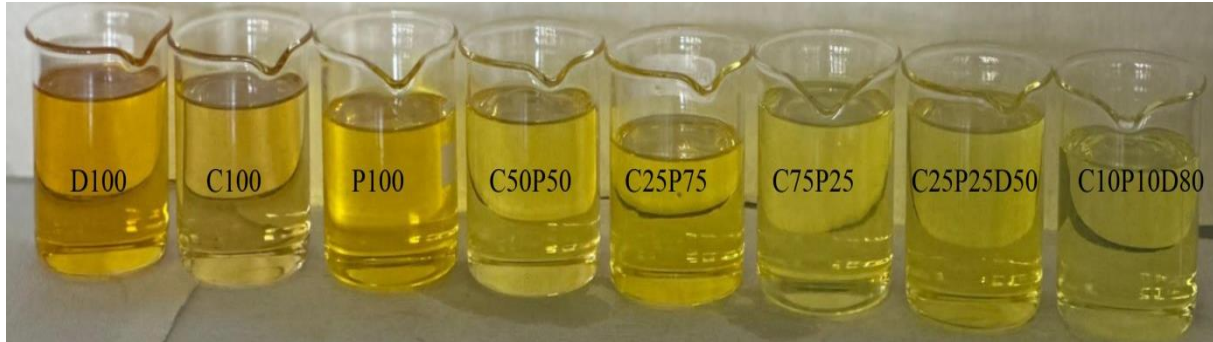


Figure 5. Prepared biodiesels and fuel blends

Determination of physicochemical properties of fuels and mixtures

In the study, the fuel analysis laboratory and the measurement devices in the laboratory, which was established within the scope of the DPT 2004/7 project (Öğüt et al., 2004) within the Department of Agricultural Machinery and Technologies Engineering, Faculty of Agriculture, Selçuk University, were used to determine the physicochemical properties (kinematic viscosity, density, calorific value, water content, flash point, cold filter plugging point, copper strip corrosion) of all fuels and blends.

The analyses of the fuels and blends were carried out according to the working methods of the devices used in the measurement (Table 2) and the results of the analyses were based on the EN 14214 European Union and ASTM D 6751 American standards applied for biodiesel today and their compliance with these standards was determined (Table 3).

Table 2. Specifications and measurement standards of test equipment

Fuel Property	Devices	Measurement Range	Unit	Measurement Accuracy	Standard
Density	Kem Kyoto DA-130N	0.0000 - 2.0000	g cm ⁻³	±0.0001	EN ISO 3675 EN ISO 12185
Kinematic viscosity	Koehler K23377	Ambient temperature – 150	°C	±0.01	EN ISO 3104
Flash point	Koehler K16270	Ambient temperature -370	°C	±0.01	EN ISO 2719 EN ISO 3679
Water content	Kem Kyoto MKC-501	10µg-100mg	µg	±0.01	EN ISO 12937
Calorimeter	IKA C 200	0-40.000	J	±0.0001	DIN 51900
Cold filter plugging point	Tanaka AFP-102	With a coolant down to -60°C	°C	±0.01	ASTMD6379
Cloud and pour point	Koehler	-	°C	-	ASTM D97
Copper strip corrosion	Koehler K 25330	0-190	°C	±0.01	EN ISO 2160

Table 3. Biodiesel Standards

Property	Unit	European Standards			American Standards	
		EN 14214	EN16709	Test Method	ASTM D 6751	Test Method
Density (at 15°C)	(g cm ⁻³)	0.86-0.90	0.82-0.86	EN ISO 3675 EN ISO 12185	-	-
Kinematic Viscosity (at 40°C)	(mm ² s ⁻¹)	3.5-5.0	2.0-4.62	EN ISO 3675 EN ISO 12185	1.9-6.0	D 445
Flash Point	(°C)	≥120	≥55	EN ISO 3104 ISO 3105	≥130	D93
Calorific Value	Mj/kg	≥38	-		37.27	D4809
Water Content	(mg kg ⁻¹)	≤500	≤260	ISO 3987	≤500	D 2709
Copper Strip Corrosion (3h/50°C)	Degree of corrosion	Class 1	Class 1	EN ISO10370	≤3	D 130
Cold Filter Plugging Point	(°C)	<-10	<-20	EN 14107	-	-
		B100	B20			

RESULTS and DISCUSSION

Some physicochemical properties values of diesel, camelina biodiesel, waste pumpkin oil biodiesel and blended fuels are given in Figure 6. The results were compared with TS EN 14214 and ASTM D 6751 standards.

Very little change was observed in the density values of C100, P100 biodiesel and C50P50, C25P75 and C75P25 binary biodiesel blends. Addition of diesel to biodiesel + biodiesel blends decreased the density values of the blend fuels. Researchers reported similar results in other studies (Eryilmaz et al., 2022; Nayak et al., 2021; Sirviö et al., 2018).

High viscosity causes poor fuel atomisation during spraying, increases carbon build-up in the fuel filter, demands more energy from the fuel pump and wears out fuel pumps and injectors (Meher et al., 2006; Tate et al., 2006). The higher viscosity causes the mixture to burn poorly in the engine due to the slow movement of the fuel through the fuel filter and fuel lines. In addition, the high viscosity of biodiesel fuel affects injection start, injection pressure and fuel spray characteristics, which are the main parameters affecting engine performance and exhaust emissions (Tesfa et al., 2010).

In this study, kinematic viscosity values of all biodiesel fuels (C100, P100, C50P50, C25P75 and C75P25) were within EN 14214 and ASTM D 6751 standards. Viscosity values of binary biodiesel blended fuels (C25P25D50 and C10P10D80) mixed with diesel were found in EN16709 and ASTM D 6751 standards. The viscosity values of C100 and P100 biodiesels were 4.58 mm² s⁻¹ and 4.32 mm² s⁻¹, respectively. The viscosity value of camelina biodiesel was higher than that of waste pumpkin seed biodiesel. The high viscosity of biodiesel is due to the high content of saturated fatty acids and long carbon chains (Ghazali et al., 2015; H. C. Ong et al., 2014; Veluru et al., 2022). The unsaturated fatty acid content of pumpkin seed oil ranges between 80-82% (Yücelşengün et al., 2021), while that of camelina oil ranges between 85-86% (Eryilmaz et al., 2022). In biodiesel+biodiesel binary fuel blends, the viscosity value increased as the proportion of camelina increased. Addition of dizle to biodiesel+biodiesel+diesel triple blends decreased the viscosity value. Similar results were reported by Habibullah et al. (2015); Swarna et al., (2022).

Flash point means the lowest temperature necessary air and fuel vapours on the fuel to burn when heated. A high flashpoint is considered suitable for storing and transporting. The flash points of all biodiesel and fuel blends were found to be within EN 14214, EN 16709 and ASTM D6751 standards. The flash point of biodiesel is also affected by its volatility; higher flash point temperatures reduce the risk of fire and make biodiesel safer to handle and store than diesel fuels (Odega et al., 2021). The flash point of biodiesel and binary biodiesel blends varied between 140 oC and 145 oC. In binary biodiesel blends, increase in diesel by volume decreased the flash point. Similar results were reported by Eryilmaz et al. (2022); Nayak et al. (2021) in their studies.

Calorific value is an important characteristic in fuel selection (Atabani and César, 2014). It is one of the most important properties to characterise a fuel (Ong et al., 2013; Silitonga et al., 2013). The presence of chemically bound oxygen explains the low calorific value of biodiesel (Mansourpoor and Shariati, 2012), whereby an increase in the oxygen content reduces the calorific value of biodiesel fuel compared to traditional petroleum-based diesel fuel. The calorific value of C100 and P100 biodiesel fuels were 11.25% and 10.33%

lower than diesel, respectively. Oxygen content in biodiesel caused the calorific value to decrease. Calorific values of C50P50, C25P75 and C75P25 binary biodiesel blends were measured as 39.4 MJ/kg, 39.52 MJ/kg and 39.29 MJ/kg, respectively. Addition of diesel to the binary biodiesel blends increased the calorific value. The reason for this can be attributed to the decrease in the oxygen content of the fuels and the increase in the calorific value accordingly. Studies in the literature also reported similar results (Ciubota-Rosie et al., 2013; Sirviö et al., 2018).

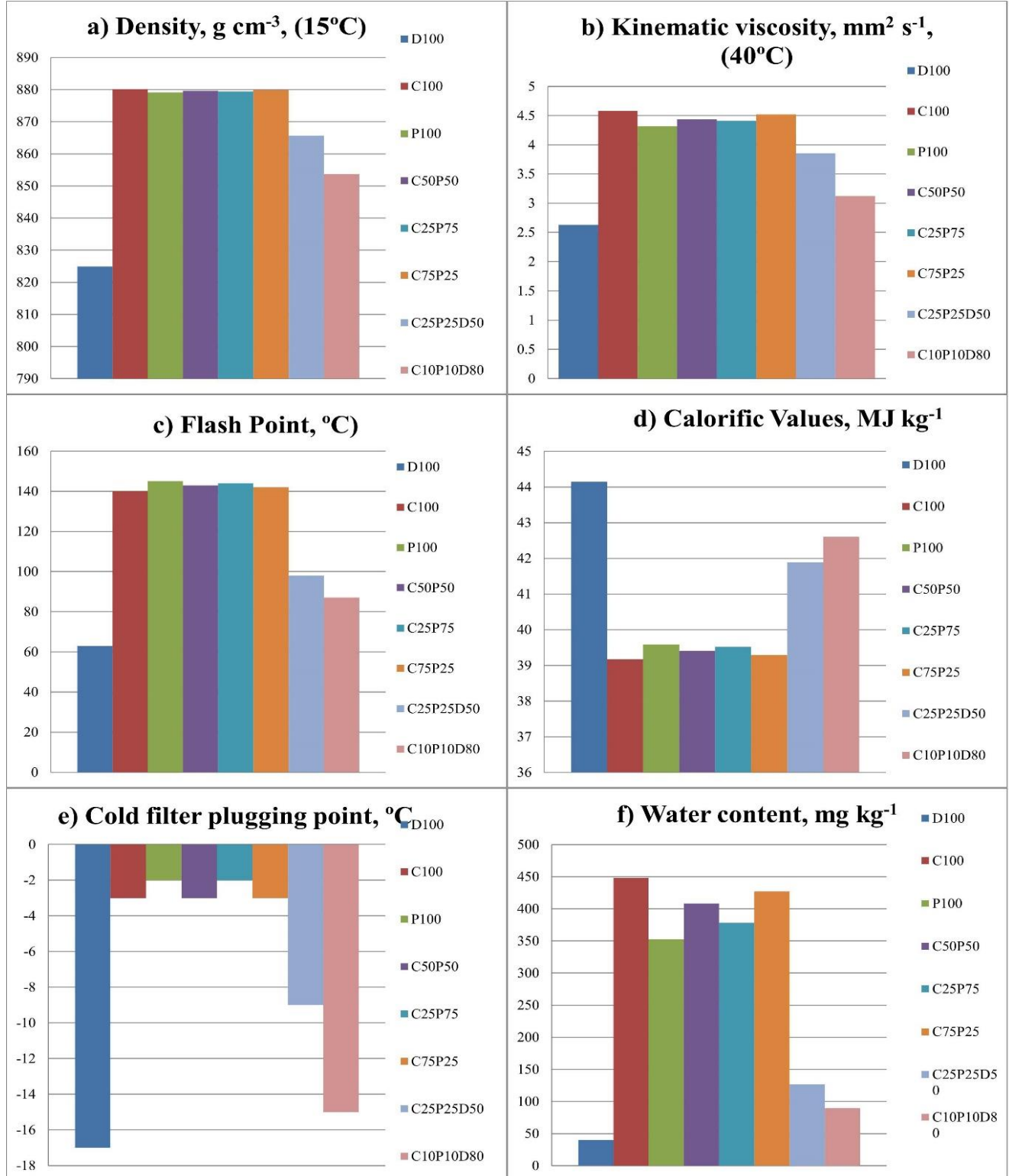


Figure 6. Fuel properties of diesel, camelina biodiesel, waste pumpkin oil biodiesel, binary biodiesel and binary biodiesel+diesel blends

CFPP determines the temperature at which fuel begins to form wax crystals, which can clog fuel lines and filters, causing engine failures (Sirviö et al., 2019). In this study, the CFPP values of C100 and P100 biodiesel were -3 °C and -2 °C, respectively. The CFPP value of C100 was lower than P100. The reason for this may be attributed to the excess of saturated fatty acids in camelina oil biodiesel. Saturated fatty acids have a higher melting point and tend to solidify at lower temperatures, resulting in poor cold flow properties (Leng et al., 2020). The increase in diesel by volume in binary biodiesel fuel blends decreased the CFPP value.

Copper strip corrosion values were determined as 1a in all fuels and were similar to Ciubota-Rosie et al. (2013); Eryilmaz et al. (2022).

The water content in biodiesel is a critical parameter that significantly affects its quality and performance. Excessive water content can result in reduced oxidation stability, reduced shelf life and potential for microbial growth, which can lead to clogging of the fuel filter and corrosion of the fuel delivery system (Jalil et al., 2022). The water contents of all fuels and blends were found to be within EN14214, EN16709 and ASTM D 6751 standards. It was determined that camelina biodiesel had 27% higher water content than waste pumpkin seed oil biodiesel. In binary biodiesel fuel blends, the increase in the volume of camelina biodiesel increased the water content. In ternary fuel blends, the increase in diesel fuel by volume and the decrease in biodiesel fuel ratios decreased the water content.


CONCLUSION and RECOMMENDATIONS

In this study, the fuel quality and relationships of biodiesel (C100) produced from camelina crude oil, biodiesel (P100) produced from waste pumpkin oil, binary biodiesel blends (C50P50, C25P75 and C75P25) and ternary fuel blends (C25P25D50, C10P10D80) were investigated.

Physicochemical properties of all fuel samples (D100, C100, P100, C50P50, C25P75, C75P25, C25P25D50, C10P10D80) were as follows; density (g cm^{-3}) (at 15 °C) 824.9; 880.2; 879.1; 879.6; 879.4; 879.9; 865.7 and 853.7, kinematic viscosity ($\text{mm}^2 \text{s}^{-1}$) (at 40 °C) 2.63; 4.58; 4.32; 4.44; 4.41; 4.52; 3.86; 3.12, flash point (°C) 63; 140; 145; 143; 144; 142; 98; 87, calorific value (Mj kg^{-1}) 44.14; 39.17; 39.58; 39.4; 39.52; 39.29; 41.88; 42.6, cold filter plugging point (°C) -17; -3; -2; -2; -3; -2; -3; -9; -15, water content (ppm) 40.15; 448.28; 352.51; 408.16; 378.06; 427.14; 126.5; 89.78, copper strip corrosion (3h at 50°C) was determined as 1a in all fuels. The values closest to diesel fuel quality were obtained in C10P10D80 triple fuel blend. According to these results, the use of binary biodiesel blends with different physicochemical properties in fuel blends with high biodiesel content (such as B20) can improve the properties of fuels.

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AUTHOR ORCID NUMBERS

Seda ŞAHİN  <http://orcid.org/0000-0003-1743-9530>

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