2

The fuel properties of methyl esters produced from canola oil- animal tallow blends by basecatalyzed transesterification

Şehmus Altun^a, Fevzi Yaşar^b and Cengiz Öner^c

^aDepartment of Mechanical Education Batman University, 72100 Batman, Turkey. ^bDepartment of Refinery and Petro-Chemistry Batman University, 72100 Batman, Turkey. ^cDepartment of Mechanical Education Firat University, 23119 Elazığ, Turkey Phone: +90 (488) 217-3675; +90 (488) 217-3539; +90 (424) 237-0000- 4231 Fax: +90 (488) 213-3026 sehmus.altun@batman.edu.tr, fevzi.yasar@batman.edu.coner54@firat.edu.tr

Abstract— Biodiesel is an alternative diesel fuel that can be produced from renewable feedstocks such as vegetable oil or animal fats by transesterification with methanol for using in diesel engines. The viscosity and density of biodiesel fuels are important parameters due to being key fuel properties for injection and combustion process of diesel engines. These fuel properties mainly depend on the feedstock which is used in the biodiesel production. In this study, the blends containing 0, 25, 50, 75 and 100% of food-grade canola oil/inedible animal tallow in volume basis were prepared and converted into methyl esters by base-catalyzed transesterification. Effect of inedible animal tallow-canola oil blends on the viscosity and density of methyl esters were investigated. Experimental results showed that the kinematics viscosity of methyl esters increased as animal tallow ratio increased in the feedstock. Besides, it was observed that density did not change much.

Index Terms— Canola oil, inedible animal tallow, Biodiesel production, Fuel properties.

I. INTRODUCTION

B iodiesel is the mono-alkyl esters of long chain fatty acids derived from renewable feedstock, such as vegetable oil or animal fats for using in compression ignition engine. Biodiesel, which is considered as a possible substitute of conventional diesel fuel, is commonly composed of fatty acid methyl esters that can be prepared from triglycerides by transesterification with methanol. The resulting biodiesel is quite similar to petroleum based diesel fuel in its fuel properties; and this fuel is biodegradable and non-toxic and has low emission profiles as compared to petroleum based diesel fuel [1,2]. The molecular structure of biodiesel is similar to diesel fuel, and it contains additional oxygen, which is useful to reduce unburned HC, CO, and smoke opacity in the exhaust. However, a diesel engine fuelled with biodiesel or its blend generally releases higher NO_x emission than that of petroleum-based diesel fuel [3]. But some studies also reported lower NO_x emissions when biodiesel fuel and its blends were used [4,5]. This may be attributed to differences in fatty acid composition of biodiesel fuels. Because fuel properties of biodiesel are affected by its fatty acids content, which may cause difference in characteristics of injection, combustion, and emissions [6]. The current use of biodiesel is related to specific climates, agricultural policies, and the environmental laws of countries [7]. In Germany and other European countries, biodiesel is usually rapeseed oil methyl ester (RME), which is derived from low-erucic acid rapeseed oil, whereas in the United States it is mainly soy methyl ester [8]. The oil of choice for the production of biodiesel in the Mediterranean area is presently the sunflower oil [9]. In Malaysia and Indonesia palm oil is used as a significant biodiesel source. In India and Southeast Asia, the Jatropha tree is used as a significant fuel source [10]. Biodiesel has over double the price of petroleum diesel. The high price of biodiesel is in large part due to the high price of the feedstock. The high cost of the food-grade oils causes the cost of biodiesel to increase and prevents its usage [10,11]. In this case, animal fats with lower cost feedstock can be preferred in biodiesel production. Therefore, animal fats having a higher cetane number that reduces the amount of fuel burnt in the premixed fraction of the combustion process, the combustion noise, and the NO_x formation are searched for [12]. However, the biodiesel produced from animal fats have poor fuel properties since they are more saturated than vegetable oils. To solve these problems, blending animal fats with vegetable oils in biodiesel production may be a good method. For instance, Canoira et al. [13] evaluated the properties of biodiesel in different mixtures of animal fat and soybean oil, and they showed that kinematics viscosity and cold-filter plugging point (CFPP) decreased with the increasing amount of soybean oil in feedstock. In the same way, the study of Taravus et al. [14] showed that physical properties of the methyl esters from sunflower oil and beef tallow blends improved positively as the beef tallow ratio decreased in the biodiesel feedstock. And it was also mentioned in their study that although beef tallow has poor properties as a feedstock in biodiesel production, it is a necessity to take advantage of it to

reduce the raw material cost, which consists of up to 70% of the total cost of biodiesel. Issariyakul et al. [15] reported that viscosity of esters decreased with a decrease in used cooking oil to canola oil ratio as used cooking oil itself was more viscous than canola oil. They also expressed that if the feedstock consists of 40% used cooking oil instead of pure canola oil, the feedstock cost will be reduced by 20%.

The objective of this study is to investigate both the biodiesel production from different blends of animal fat and vegetable oil and their effects on fuel properties. In this study, biodiesel fuels were produced from inedible animal tallow and food-grade canola oil blends by base-catalyzed transesterification, and their fuel properties such as viscosity and density were investigated.

II. MATERIALS AND METHODS

The inedible animal tallow was purchased from city slaughterhouse of Elazığ, Turkey. The inedible animal tallow used in this study is a mixture of slaughtered cattle and sheep fats, and that these fats were marketed for soap production. Before transesterification, animal tallow was heated at 105-110 °C for 1 h and then the sediment was strained out of the tallow with cloth filter. Impurities and bubbles formed on surface of tallow were picked during heating process. The food-grade canola oil used in this study was purchased from a local market, which was refined and winterized. The foodgrade canola oil used in this study did not need to be filtered prior to transesterification as is required for the inedible animal tallow. The experimental studies performed with a sample of 600 g of feedstock which was placed in a 1000 ml flat-bottom flask equipped with a magnetic stirrer-heater, digital thermometer and condenser. The methanol (99.7% purity) and NaOH (98% purity) were used in the transesterification. As the catalytic activity of a base is higher than that of an acid, and acid catalysts are more corrosive, the base-catalyzed process is preferred to the acid-catalyzed one, and is thus most often used commercially [18]. The transesterification of canola oil and its blends with inedible animal tallow was carried out using ratio of methanol to feedstock of 20% by volume and about 0.8 wt.% catalyst. Since biodiesel production was experimental procedure, we followed the procedure which is shown in Figure 1. The inedible animal tallow was heated to 60°C gradually and then canola oil was added into it. In another beaker, methanol and sodium hydroxide were mixed, until all NaOH was dissolved in methanol. Afterwards, this mixture was added into the feedstock mixture of inedible animal tallow and canola oil, and stirred rigorously, and heated further to 60°C for 1 h. When the reaction reached the present reaction time, heating and stirring were stopped. The methyl esters phase separated from the bottom glycerol phase was then washed by warm distilled water. The fatty acid distribution of canola oil methy ester and inedible tallow methyl ester was obtained from Moser, B.R [16] and Ali et al. [17] and presented in Table 1. According to Table 1, the animal tallow methyl ester's saturated fatty acid amount is 39.34% while canola oil methyl ester is 7.7% saturated. This can be significant when considering as a diesel engine fuel of the biodiesel since saturation level has an effect on fuel properties. Kinematics viscosity (at 40 °C) and density (at 15 °C) of methyl esters were determined in TÜPRAŞ (Turkish Petroleum Refineries Co.) Batman Refinery, fuel analyze laboratory using analysis instruments according to related ASTM standards. The measurements were done by using Herzog (HVM 472) viscosity meter and Anton Paar (DMA 5000) density meter.

 Table 1. Major fatty acids (wt%) in inedible tallow and canola oil methyl esters

Fatty Acids	Canola Oil Methyl Ester	Inedible Tallow Methyl Ester
	(%)	(%)
C16:0	4.6	23.76
C18:0	2.1	13.79
C18:1	64.3	48.18
C18:2	20.2	9.88
C18:3	7.6	-
Saturated	7.7	39.34
unsaturated	92.3	60.66



Figure 1. Biodiesel production process

III. RESULTS AND DISCUSSIONS

A. The kinematics viscosity

The viscosity of an engine fuel is one of the most critical fuel features. It plays a dominant role in the fuel spray, mixture formation and combustion process [11]. Viscosity affects the atomization of a fuel upon injection into the combustion chamber and thereby ultimately the formation of engine deposits. The higher the viscosity is, the greater the tendency of the fuel is to cause such problems [19]. The viscosity of neat vegetable oils and fats is much higher than that of diesel fuel. Transesterifying oils or fats to the corresponding alkyl esters reduce viscosity by almost an order of magnitude [20]. The viscosity of biodiesel fuels from different sources are generally higher than that of petroluem diesel fuel. The variation of kinematics viscosity with the increase of canola oil ratio in the feedstock is presented in Fig. 2. The kinematics viscosity in biodiesel standards has been determined as 1.9-6.0 mm²/s in ASTM D 6751 and 3.5-5.0 mm²/s in EN 14214. The kinematics viscosity of methyl esters in this study was within the given standards. The kinematics viscosity was less for biodiesels from canola oil and its blends with inedible animal tallow than for the inedible animal tallow biodiesel alone, as shown in Fig. 2. Canola oil methyl ester had the lowest viscosity, while animal tallow methyl ester had the highest. It has been reported by Lin and Li [21] that the larger proportions of saturated fatty acids with longer carbon chains cause kinematics viscosity to increase. Thus, the inedible tallow methyl ester which contained 39.34 wt.% saturated fatty acids, appeared to have greater kinematics viscosity, whereas those of canola oil methyl esters are 7.7 wt.%, as seen in Table 1. Wyatt et al. [22] founded that viscosities for the animal fat-derived fatty acid methyl ester, in general, were slightly higher than that for the soy-based esters but were within the specified limit. Knothe [23] also reported that biodiesel fuels derived from used frying oils tend to possess higher viscosity than those from most vegetable oils, owing to their higher content of trans FA and saturated. Thereby, lower viscosity of methyl esters from canola oil and blends with respect to inedible animal tallow can be attributed to saturation level. But it was reported by Wyatt et al. [22] that there was no correlation between the saturated fatty ester content of the esters and viscosity. Also, in this study, it was not observed a linear increase with the amount of animal tallow ratio in the feedstock. Namely, the viscosity of the blended feedstocks was almost similar to each other. As a result, it can be said that the viscosity was positively influenced when the canola oil was blended with inedible animal tallow for the biodiesel production.

B. The density

The density is an another important property of biodiesel. It is the weight of a unit volume of fluid. Fuel injection equipment operates on a volume metering system, hence a higher density for biodiesel results in the delivery of a slightly greater mass of fuel [24]. The density in biodiesel standards has been determined as 860-890 kg/m³ in EN 14214. In this study, the density of biodiesels produced is between these values. Inedible animal tallow methyl ester has slightly lower density among the methyl esters and the densities of the others are close to each other, as shown in Fig. 3. As reported by Alptekin and Çanakçı [25] density of biodiesel fuels has not changed much, because the densities of methanol and oil are close to the density of the produced biodiesel. The density of vegetable oil based methyl esters from different sources reported in many studies is very close to each other (around 880 kg/m³), whereas animal fat based methyl esters have density of around 870 kg/m³ [13,25,26,27]. Although these values are in accordance with the standards, they are slightly higher than those of the petroleum based diesel fuels. On the other hand, densities of biodiesel fuels will vary with the fatty acid composition and their purity [25;28]. For instance, it was reported by Yahya and Marley [29] that the specific gravity decreased slightly with increased saturation in the ester composition.



Fig. 2. The variation of viscosity with canola oil increased in the biodiesel feedstock



Fig. 3. The variation of density with canola oil increased in biodiesel feedstock

In the same way, Graboski et al. [30] also reported that more saturated esters have higher cetane numbers and lower densities than less saturated esters. In this study, also, the animal tallow methyl ester which contained more saturated fatty acids has slightly lower density than those of other methyl ester. Eventually, the change of the density obtained in this study agrees well with the effect above.

IV. CONCLUSION

Biodiesel is an alternative diesel fuel that can be produced from renewable feedstocks such as vegetable oil or animal fats by transesterification with methanol for using in diesel engines. The viscosity and density of biodiesel fuels are important parameters due to being key fuel properties for injection and combustion process of diesel engines. These fuel properties mainly depend on the feedstock which is used in the biodiesel production. In this study, the biodiesel fuels from different blends of canola oil and inedible animal tallow were produced and the fuel properties were investigated. The viscosity was positively influenced when canola oil was increased in the feedstock. Besides, the density of biodiesel fuels have not changed much.

V. REFERENCES

- Meher, L.C. Vidya Sagar, D. Naik, S.N. "Technical aspects of biodiesel production by transesterification—a review", *Renewable and Sustainable Energy Reviews*. 10, 248–268, 2006.
- [2] Srivastava, A. Prasad, R. "Triglycerides-based diesel fuels", *Renewable and Sustainable Energy Reviews*. 4, 111-133, 2000.
- [3] Özsezen, A.N. Çanakçı, M. and Sayın, C. "Effects of Biodiesel from Used Frying Palm Oil on the Exhaust Emissions of an Indirect Injection (IDI) Diesel Engine", *Energy & Fuels*. 22, 2796–2804, 2008.
- [4] Öner, C. Altun, Ş. "Biodiesel production from inedible animal tallow and an experimental investigation of its use as alternative fuel in a direct injection diesel engine", *Applied Energy*, 86, 2114–2120, 2009.
 [5] Yamık, H. İçingür, Y. "Bir dizel motorunda ayçiçek yağı esterlernin
- [5] Yamık, H. Içingür, Y. "Bir dizel motorunda ayçiçek yağı esterlernin yakıt olarak kullanılmasının performans ve emisyonlara etkisi", *Teknoloji*, 11(3), 201-209, 2008.. (in Turkish).
- [6] Özsezen, A.N. Çanakçı, M. and Sayın, C. "Effects of Biodiesel from Used Frying Palm Oil on the Performance, Injection, and Combustion Characteristics of an Indirect Injection Diesel Engine", *Energy & Fuels*, 22, 1297–1305, 2008.
- [7] Lin, B-F. Huang, J-H, and Huang, D-Y. "Effects of Biodiesel from Palm Kernel Oil on the Engine Performance, Exhaust Emissions, and Combustion Characteristics of a Direct Injection Diesel Engine", *Energy* & Fuels, 22, 4229–4234, 2008.
- [8] Krahl, J. Bünger, J. Schröder, O. Munack, A. and Knothe, G. "Exhaust Emissions and Health Effects of Particulate Matter from Agricultural Tractors Operating on Rapeseed Oil Methyl Ester", *JAOCS*, 79 (7), 717-724, 2002.
- [9] Lapuerta, M. Armas, O. Ballesterosa, R. Fernandez, J. "Diesel emissions from biofuels derived from Spanish potential vegetable oils", *Fuel*, 84, 773–780, 2005.
- [10] Demirbaş, A. "Importance of biodiesel as transportation fuel", *Energy Policy*, 35, 4661–4670, 2007.
- [11] Çanakçı, M. Şanlı, H. "Biodiesel production from various feedstocks and their effects on the fuel properties", *J Ind Microbiol Biotechnol*, 35:431– 441, 2008.
- [12] Lapuerta, M. Rodriguez-Fernandez, J. Oliva, F. and Canoira, L. "Biodiesel from Low-Grade Animal Fats: Diesel Engine Performance and Emissions", *Energy & Fuels.* 23, 121–129, 2009.
- [13] Canoira, L. Rodriguez-Gamero, M. Querol, E. Alcantara, R. Lapuerta, M. and Oliva, F. "Biodiesel from Low-Grade Animal Fat: Production Process Assessment and Biodiesel Properties Characterization", *Ind. Eng. Chem. Res.* 47, 7997–8004, 2008.
- [14] Taravus, S. Temur, H and Yartaşı, A. "Alkali-Catalyzed Biodiesel Production from Mixtures of Sunflower Oil and Beef Tallow", *Energy & Fuels*, 23 (8), 4112–4115, 2009.
- [15] Issariyakul, T. Kulkarni, M.G. Meher, L.C. Dalai, A.K. Bakhshi, N.N. "Biodiesel production from mixtures of canola oil and used cooking oil", *Chemical Engineering Journal*, 140, 77–85, 2008.
- [16] Moser, B.R. "Influence of Blending Canola, Palm, Soybean, and Sunflower Oil Methyl Esters on Fuel Properties of Biodiesel", *Energy & Fuels*, 22, 4301–4306. 2008.
- [17] Ali, Y. Hanna, M.A. and Cuppett, S.L. "Fuel Properties of Tallow and Soybean Oil Esters", *JAOCS*, 72 (12), 1557-1564, 1995.
- [18] İlgen, O. et al. "Investigation of Biodiesel Production from Canola Oil using Mg-Al Hydrotalcite Catalysts", *Turk J Chem*, 31,509–514, 2007.

- [19] Knothe, G."Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters", *Fuel Processing Technology*, 86, 1059–1070. 2005.
- [20] Knothe, G. Steidley, K.R. "Kinematic viscosity of biodiesel components (fatty acid alkyl esters) and related compounds at low temperatures", *Fuel*,86 (16), 2560-2567, 2007.
- [21] Lin, C-Y. Li, R-J. "Fuel properties of biodiesel produced from the crude fish oil from the soapstock of marine fish", *Fuel Processing Technology*, 90, 130–136, 2009.
- [22] Wyatt, V.T. Hess, M.A. Dunn, R.A. Foglia, T.A. Haas, A.J. and Marmer, W.N. "Fuel Properties and Nitrogen Oxide Emission Levels of Biodiesel Produced from Animal Fats", *JAOCS*, 82(8), 585-591, 2005.
- [23] Knothe, G. "Analyzing Biodiesel: Standards and Other Methods", JAOCS, 83(10), 823-833, 2006.
- [24] Demirbaş, A.Karslıoğlu, S."Biodiesel Production Facilities from Vegetable Oils and Animal Fats"*Energy Sources, Part A*,29,133–141, 2007.
- [25] Alptekin, E. Çanakçı, M. "Determination of the density and the viscosities of biodiesel- diesel fuel blends", *Renewable Energy*, 33, 2623–2630. 2008.
- [26] Graboski, M.S. and Mccormick, R.L. "Combustion of Fat and Vegetable Oil Derived Fuels in Diesel Engine", *Progress Energy Combustion Science*, 24, p.125-164, 1998.
- [27] da Cunha, M.E. et al. "Beef tallow biodiesel produced in a pilot scale", Fuel Processing Technology. 90(4), 570–575, 2009.
 [28] Tat, M.E. Van Gerpen, J. "The specific gravity of biodiesel and its
- [28] Tat, M.E. Van Gerpen, J. "The specific gravity of biodiesel and its blends with diesel fuels", JAOCS, 77(2), 115–119, 2000.
- [29] Yahya, A. Marley, S.J. "Physical and Chemical Characterization of Methyl Soyoil and Methyl Tallow Esters as CI Engine Fuels", *Biomass* and Bioenergy, 6 (4), 321-328, 1994.
- [30] Graboski, M.S. "Effect of Biodiesel Composition on NO_x and PM Emissions from a DDC Series 60 Engine", *Final Report to National Renewable Energy Laboratory*, Contract No. ACG-8-17106-02. December 29, 1999.