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Derya Unlu, Nezahat Boz, Oguzhan Ilgen, Nilufer Hilmioglu*

Improvement of fuel properties of biodiesel with bioadditive ethyl levulinate

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Abstract: Biodiesel has poor cold flow properties due to their high saturated fatty acid content. Ethyl levulinate is used as bio-based cold flow improver additive in biodiesel. In this work, both ethyl levulinate and biodiesel were synthesized in the laboratory. Ethyl levulinate was added to the biodiesel at different rates, i.e, 5, 10, 15, 20 (vol %). The effect of ethyl levulinate addition on density, kinematic viscosity, acid value, cloud point and pour point was determined and compared to the EN 14214 and ASTM D6751 specification. Consequently, ethyl levulinate appears acceptable as a cold flow improver for biodiesel fuel.

Keywords: Biodiesel; Cold flow improver; Ethyl levulinate; Fuel bioadditive; Renewable energy.

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1 Introduction

Biofuel production from biomass is an important alternative energy source, so the conversion of waste biomass to raw materials and valuable biofuels / bioadditives has ever increasing interest in recent years. Compared to fossil fuels, biofuels have low sulfur content and reduce the CO_2 emissions. Therefore, they don't cause acid rain and have low harmful effects to the environment [1]. Besides that, they can be used directly or blended in the diesel engine without any modification. However, differences in the chemical compositions affect the engine performance and emission properties [2-4].

Biodiesel is the most popular alternative biofuel for the transport and fuel sector. Biodiesel can be produced from vegetable oil, animal oil/fats and various waste materials, and it can be used in diesel engines without modifications [5-7]. The biodiesel is called "green fuel" due to its biodegradable, renewable, non-toxic and environmental friendly properties [8-12]. However, there are also some disadvantages to the use of biodiesel in cold climates such as its higher viscosity, cloud point and pour point. For example, the higher viscosity value of biodiesel results in poor atomization qualities, and low combustion quality. Also, injector coking, ring sticking and gumming in diesel engines have been seen at the high viscosity levels [3]. To overcome these problems, utilization of fuel additives is required. In this regard, ethyl levulinate (EL) derived from biomass has been suggested as a potential fuel additive. EL was considered a bio-based cold flow improver for biodiesel fuels, because EL has a lower cloud point than biodiesel, resulting in better general cold flow properties. It also has excellent properties such as clean combustion and low toxicity according to the other oxygenates for fuel additive [13, 14]. Ethyl levulinate is a colourless or light yellow liquid. The density of EL at 25°C is 1.06 kg/m^3 and kinematic viscosity is 1.50 mm^2/s. The cloud point of EL is -5°C and pour point is -13°C [15].

The highlight of this study and main difference from the literature is the synthesis of ethyl levulinate for use as a fuel bioadditive. In the only study in literature about the fuel properties of ethyl levulinate, ethyl levulinate was supplied from MeadWestvaco Corp by Joshi et al [16]. In order to obtain high yield and high purity of ethyl levulinate, ethyl levulinate synthesis was carried out in a pervaporation membrane reactor. In addition, while the biodiesel was produced from cottonseed oil in literature, it was synthesized from the canola oil in this study. There is no study in the literature where both of ethyl levulinate and biodiesel are synthesized under laboratory conditions and the fuel properties of this binary mixture examined.
In brief, the aim of this study was to investigate the effects of some fuel properties of blending EL with canola oil methyl esters. Using standard methods, density, kinematic

***Corresponding author: Nilufer Hilmioglu,** Kocaeli University, Chemical Engineering Department, Kocaeli, Turkey, E-mail: niluferh@kocaeli.edu.tr
Derya Unlu, Oguzhan Ilgen: Kocaeli University, Chemical Engineering Department, Kocaeli, Turkey
Nezahat Boz: Gazi University, Chemical Engineering Department, Ankara,Turkey

viscosity, acid value, cloud point and pour point were determined. Comparison of the obtained results of blending biodiesel with EL to biodiesel fuel standards was examined.

2 Experimental

2.1 Materials

Methanol and potassium hydroxide (KOH) were all purchased from Merck Chemicals. Commercial canola oil was purchased from a local food market.

2.2 Synthesis of ethyl levulinate

The synthesis of the EL by using pervaporation catalytic membrane reactor with catalytic composite membrane was adapted from reference [17].

Ethyl levulinate was synthesized with esterification of levulinic acid with ethanol in a pervaporation catalytic membrane reactor. Sulfated zirconia loaded catalytic composite hydroxyethyl cellulose membrane was used in the system. Composite membrane has catalytic and separation layer. Composite membrane was placed in the reactor. Levulinic acid and ethanol as reactants were fed to the reactor by a feed pump and contact the catalytic layer of the membrane. Reactants are converted to products 'ethyl levulinate and water' in the catalytic layer of the membrane. While the water was permeated through the separation layer of the membrane due to the hydrophilic properties of hydroxyethyl cellulose, unconverted reactants and ethyl levulinate diffused back to reaction medium from the top surface of the membrane. Water was diffused through the membrane as the vapor phase because of the reduced pressure in the permeate side of the membrane and collected in the cold trap. Vapor was condensed in liquid nitrogen and obtained as liquid. Samples from the reaction medium and permeation were taken hourly and concentration of components was determined by using gas chromatography.

2.3 Biodiesel production

The conversion of the canola oil to biodiesel is a transesterification reaction of the triglycerides to fatty acid methyl esters. The reaction was carried out in a 1000 mL batch reactor equipped with a reflux condenser, a magnetic stirrer and a temperature controller. Initially, KOH catalyst and methanol were mixed and then canola oil was added to the reaction mixture. The system was heated to the reaction temperature under stirring at 800 rpm. Experiments of biodiesel synthesis were carried out under atmospheric pressure. Canola oil and methanol with a 6:1 methanol to oil molar ratio and 1.5 wt% of catalyst in oil were filled into the batch reactor. The reaction time is 5 hours. At the end of the reaction, the reaction mixture was cooled to room temperature. After the removal of excess methanol, the reaction mixture is poured into a separator funnel. It was kept constant overnight. Two phases are formed as biodiesel and glycerol. The upper phase is biodiesel and biodiesel is washed with water to remove the residuals. The bottom layer is glycerol. The content of the methyl ester in the biodiesel phase was analysed by using the gas chromatography.

Ethical approval: The conducted research is not related to either human or animals use.

3 Results And Discussion

3.1 Preparation and characterization of biodiesel samples

Biodiesel production is carried out in batch reactor. At the end of the 5 h reaction, yield of biodiesel is greater than 96% for each biodiesel synthesis reaction.

3.2 Fuel properties of ethyl levulinate blended with biodiesel

The fuel properties of the fuel mixture were investigated with addition of 5%, 10%, 15% and 20% by v/v EL as a biodiesel additive. In this study, fuel properties such as the density (15°C) (EN ISO 12185), viscosity (40°C) (EN ISO 3104), acid value (EN 14104), pour point (ISO 3016) and cloud point (ASTM D2386) were characterized and interpreted in accordance with the standards. The biodiesel parameters were tested according to procedures described in the EN 14214 and ASTM D6751 standards.
Fuel property tests and measurements were repeated three times. This means, each fuel property was analyzed three times and the mean value was calculated. Mean values are given in the Figures. The repeatability of fuel properties were also within ±1%.

3.2.1 Density

Density is an important fuel property for biodiesel. The density measurements (15°C) were performed according to the EN ISO 12185 analysis method. According to this standard, the density value of biodiesel should be between 860-900 kg/m^3. The Figure 1 shows the density values obtained by the addition of different concentration of EL.

As a result, the density value given in Figure 1 was between 882.1-905.5 kg/m^3. Density of biodiesel depends on the methyl esters concentration and contamination of biodiesel [18]. As the amount of EL increased, the density of the mixture increased. This situation is an expected result since EL(1016 kg/m^3) has a higher density than biodiesel. The increase of the fuel mixture density with increasing EL amount in the fuel was also noted in the literature [19]. When the volume of 20% EL was added to fuel, the density value was found to be non-standard. Fuel injection equipment perform on a volumetric flow system, therefore higher density of biodiesel results in the consumption of greater amount of fuel [20]. Therefore, a maximum addition of 15% EL was found as suitable according to standards. Density of the fuel influences the consumption of fuel, combustion heat and exhaust emissions. High density fuel causes an increase in particulate and NOx emissions. Low density of fuel provides to form good mixing. The increment of the density value is not a problem when it is between the standard values [21, 22].

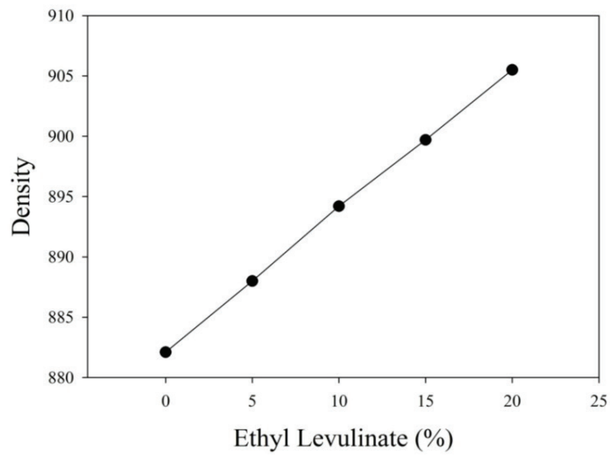

Figure 1: Effect of ethly levulinate amount on the density of the fuel mixture.

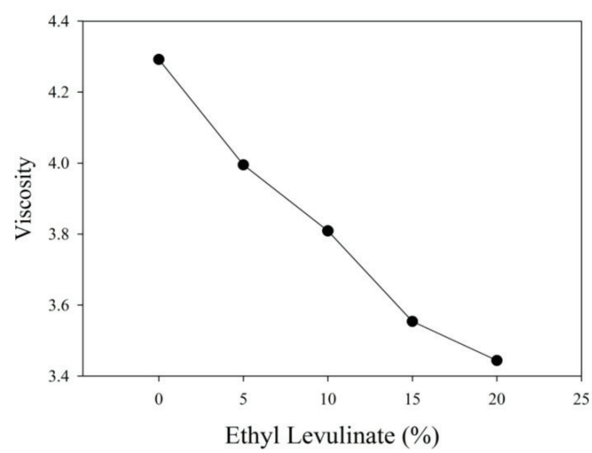

Figure 2: Effect of ethly levulinate amount on the viscosity of the fuel mixture.

3.2.2 Kinematic viscosity

Kinematic viscosity measurement (40°C) was made according to the EN ISO 3104 analysis method. According to this standard, the kinematic viscosity value of biodiesel should be between 3.5 and 5 mm^2/s. Figure 2 presents the variations in viscosity value versus EL amount.

Viscosity is the most important feature of biodiesel. It is a measure of the resistance of a liquid to flow [20]. High viscosity values of fuel has a negative effect in cold weather conditions. Viscosity is higher in value in low temperature [18].

The addition of 20% v/v EL is found as nonstandard. In this case, 15% v/v EL was found as a maximum value in accordance with the standards for kinematic viscosity. Kinematic viscosity values decreased with the addition of EL at all mixing ratios. As the addition of EL increased, the kinematic viscosity decreased. This is an expected result since EL has a lower kinematic viscosity value (1.50 mm^2/s) than biodiesel (4.292 mm^2/s) [16]. High viscosity makes mixing difficult between the fuel and air, therefore, full combustion does not occur [23]. The high viscosity value of biodiesel also prevents its use in the engine directly, and damages engine parts and the fuel system. The fluidity of fuel is very important for the fuel feed system. Atomization in cylinders is very difficult for the fuels with high viscosity. This state affects the combustion performance of the fuel and leads to decrement in thermal efficiency. High viscosity leads to accumulation of solid particles and plugging of the injectors. The high viscosity requires higher pump pressure and more energy is needed to pump the fuel, which causes wearing of the fuel pump. However, the low viscosity value of biodiesel causes weak lubrication and this insufficient lubrication results in wear and leakage [18]. All of these affect the combustion and engine performance of the fuel [22-26]. When the viscosity value is within the standards, it is not a problem in fuel properties [21].

3.2.3 Acid number

The acid number measurements (15°C) were performed according to the EN 14104 analysis method. Acid number of biodiesel, according to this standard is 0.5 mg KOH/g as maximum. Figure 3 shows the changes of acid number value with addition of EL in the fuel mixture.

When the 15-20% EL was added to biodiesel, acid number values of blends were nonstandard. A maximum addition of 10% EL was found as suitable according to standards for the acid number. As the addition of EL increased, the acid number increased. The acid number of EL is given as 0.36 mg KOH/g in the literature [16]. This value is higher than the number of acid number of pure biodiesel. Therefore, as the amount of EL increases, the value of acid number increases. In addition, the canola oil, which was used in the synthesis of canola oil methyl ester, has a higher acid number than other vegetable oils. Furthermore, the addition of EL in biodiesel increases the acidity. The increase in the number of acids results in the accumulation of solid particles in the fuel system and some problems in the filters and pumps. Free fatty acids can cause motor corrosion [27].

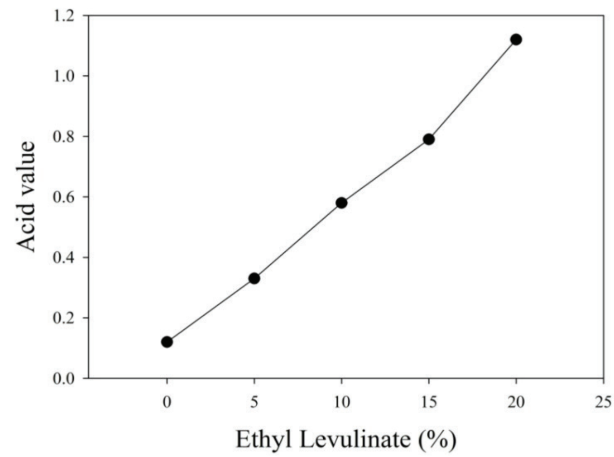

Figure 3: Effect of ethly levulinate amount on the acid value.

3.2.4 Pour point

The pour point measurements were performed according to the ISO 3016 analysis method. The pour point value of biodiesel, according to this standard is 0°C as maximum. The pour point of biodiesel/ethyl levulinate mixture for different ethyl levulinate amount is shown in Figure 4.

The lowest temperature at which movement is observed on the biodiesel is found to be the pour point [28]. While the pour point of pure biodiesel was -15°C, the pour point of biodiesel with the additive of ethyl levulinate was -12°C. The pour point was increased by the addition of ethyl levulinate. However, it was seen that there was no effect on pour point as the percentage of ethyl levulinate changed. The pour point remains constant for the addition of each concentration of ethyl levulinate. It was observed that the pour point slightly increased with the addition of ethyl levulinate. However, this value is acceptable due to the being below the maximum value.

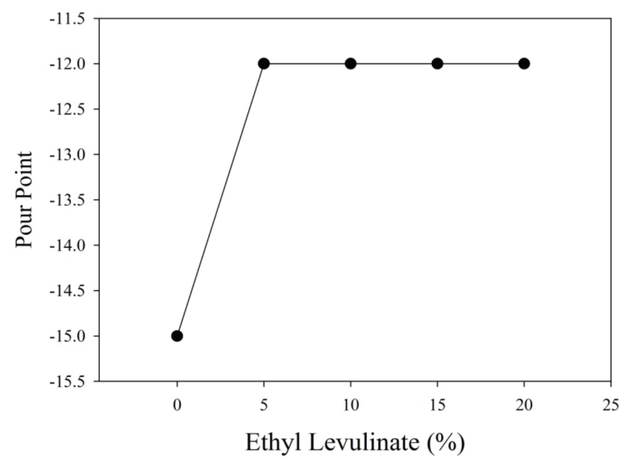

Figure 4: Effect of ethly levulinate amount on the pour point.

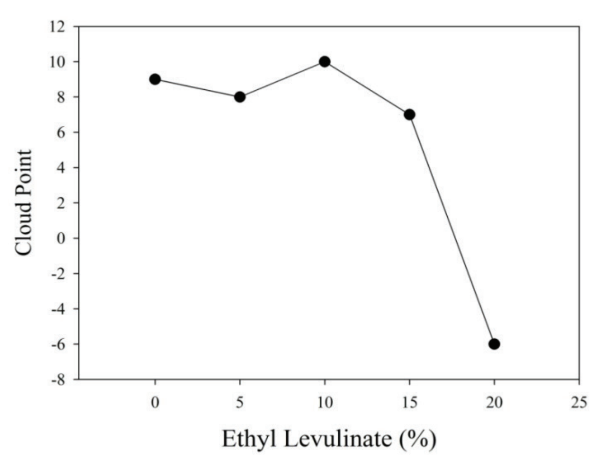

Figure 5: Effect of ethly levulinate amount on the cloud point.

3.2.5 Cloud Point

The cloud point measurements were performed according to the ASTM D 2386 analysis method. According to this standard, the cloud point value of biodiesel should be between 5°C and -65°C. Figure 5 presents the cloud point values under different ethyl levulinate amounts.

The disadvantage of biodiesel is high cloud point. All of biodiesel fuels have a high cloud point and these poor cold flow properties are the most important barrier for the use of biodiesel, so it is not suitable for cold climates. The cloud point is the temperature at which a solid suspension forms or freezes. When the fuel is cooled, wax forms at the cloud point temperature [20]. Therefore, decrement of cloud point is very important for biodiesel. The high cloud point causes the formation of crystals in the fuel at cold climatic conditions. These crystals are responsible for the plugging of fuel pipes and filters. As the concentration of ethyl levulinate increased, the cloud point decreased. This can be explained by the fact that ethyl levulinate has a lower cloud point (-79°C). This value is much lower than the cloud point of biodiesel. The canola oil contains a high percentage of saturated fatty acid methyl esters, resulting in high cloud point. Especially, decrement of cloud point is observed with the addition of 20 vol.% ethyl levulinate. The addition of ethyl levulinate reduced the cloud point of biodiesel. In particular, the addition of 20 vol.% ethyl levulinate is suitable for reducing the freezing point to -6°C [16, 28].

4 Conclusion

Recently, a novel fuel bioadditive "ethyl levulinate", which has cold flow improvement properties, has attracted considerable attention in the biodiesel sector. In this work, fuel properties of biodiesel blended with ethyl levulinate were analyzed. The blend contains 5, 10, 15 and 20% ethyl levulinate (v/v). Ethyl levulinate affects the fuel colligative properties. The density of the mixture increased upon addition of ethyl levulinate. The blended biodiesel became less viscous with increasing ethyl levulinate amounts. The acid number of biodiesel increased upon blending with ethyl levulinate. The pour point was increased by the addition of ethyl levulinate to 5 vol.%, but after that it remains constant for each subsequent addition. The blending with ethyl levulinate has improved the cold flow performance of the biodiesel. The cloud point decreased with the addition of 20 vol. % ethyl levulinate. All fuel properties of blended fuel are in standard values. This work will assist in the evaluation of ethyl levulinate to improve the cold flow properties of biodiesel fuel. The addition of 20 vol.% ethyl levulinate is an appropriate value for the addition of ethyl levulinate because maximum cold flow improver value was obtained. The mixing with ethyl levulinate improves the cold flow performance of biodiesel. In order to improve the quality of biodiesel, it is possible to use ester 'ethyl levulinate'.

Conflict of interest: Authors state no conflict of interest.

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