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# Density, flash point and heating value variations of corn oil biodiesel–diesel fuel blends

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ABSTRACT

In this study, densities of produced corn oil biodiesel and its blends with commercially available petro-diesel fuel have been investigated. The effects of temperature (T) and biodiesel percentage in blend (X) on the densities of blends were examined. The blends (B5, B10, B15, B20, B50 and B75) were prepared on a volume basis and their densities were measured by following ISO test method at temperatures of 10, 15, 20, 30 and 40 ° C. New one- and two-dimensional equations were fitted to the measurements for identifying of variations of densities with respect to X and T; and these equations were compared with other equations published in literature. Moreover, the qualities of the corn oil biodiesel and its blends were evaluated by determining the other important properties such as flash point temperature and higher heating value. In order to predict these properties, some equations were also evaluated as a function of biodiesel percentage in blend.



## 1. Introduction

Rapid depletion of known reserves and rising prices of fossil fuels, and stringent regulations on exhaust emissions have contributed to research new and clear renewable alternative fuels. Biodiesel is receiving increasing attention day by day as an alternative fuel for diesel engines [1,2]. It can be produced from renewable sources such as virgin or even used vegetable oils and animal fats via a reaction known as transesterification [3]. In this reaction, the saturated and unsaturated fatty acids in oils react with a mono-alcohol (most commonly methanol or ethanol) in the presence of a catalyst (alkali, acidic or enzyme) to yield glycerol and mono-alkyl methyl/ethyl esters (i.e. biodiesel) [4,5]. Biodiesel has already entered the fuel market and has many advantages as: (i) it comprises of 10 to 12% oxygen by mass in the molecular structure, thus improving combustion efficiency and decreasing emissions of carbon monoxide (CO), unburned or half-burned hydro carbons (HC) and smoke [6], (ii) it reduces net carbon dioxide ($CO_2$) emissions by 78% on a life-cycle basis when compared to diesel fuel [7], (iii) it is biodegradable and non-toxic, being beneficial for reservoirs, lakes, marine life and other environmentally sensitive places [8], (iv) its flash point temperature is higher than that of petro-diesel fuel (hereafter referred to as diesel fuel), which makes it less volatile and safer regarding the storage and transport than diesel fuel [9], (v) it does not contain sulphur or aromatic compounds and thus it contributes to the reduction of the diesel engine exhaust emission levels [10,11], (vi) it enhances cetane number, which shortens ignition delay [12], (vii) it can be produced by using domestic renewable feedstock, reducing country's dependency on foreign fuel supplies [13], (viii) biodiesel–diesel fuel blends or even pure biodiesel can be used in diesel engines with small modifications [14], and (viii) it improves the lubricity, which results in longer engine component life [15].

These properties of biodiesel make it an ideal fuel for diesel engines. However, there are some disadvantages of biodiesel such as lower energy content and volatility, higher viscosity and $NO_x$ emissions compared to diesel fuel [16,17]. Also, the biodiesel produced from oils, no matter if it is neat vegetable oil or animal fat, is usually more expensive than diesel fuel from 10% to 50%. Therefore, the high cost of biodiesel is the major obstacle for its commercialization [18].

Density, on the other hand, is one of the key properties since some other crucial fuel properties such as cetane number and heating value are related to it. In addition, because the amount of fuel injected to combustion chamber is measured volumetrically for diesel engines, the variation of the density directly affects the engine output power and fuel consumption. Also, density influences the start of injection, injection pressure, and fuel spray characteristics, so that these affect the combustion and exhaust emissions [15,19].

As the use of biodiesel becomes more widespread, researchers have shown a strong interest in modeling the combustion process in the engine in order to understand the fundamental characteristics of biodiesel combustion [20]. They often use physical properties of biodiesel as input data in their combustion models. However, it may not be practical at every turn to make measurements of physical properties of biodiesel or biodiesel–diesel fuel blends for each blending ratio or temperature in any study. Regression equations as a function of

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**Nomenclature and units**

a, b, d, e Regression constants
B5, B10, B15, B20, B25, B50, B75 biodiesel–diesel fuel blends
B100 pure corn oil biodiesel
D pure diesel fuel
HHV higher heating value (kJ/kg)
$K_{ball}$ coefficient of the viscometer ball (mPa · s · cm$^3$/g · s)
$m_{total}$ mass of the pycnometer filled with biodiesel (g)
R correlation coefficient
t falling time of the viscometer ball (s)
T temperature (° C)
$w_1, w_2, w_3, \ldots, w_n$ uncertainties of independent variables
$x_1, x_2, x_3, \ldots, x_n$ independent variables
X volumetric biodiesel percentage in blend (%)

*Greek symbols*
ρ density (kg/m$^3$), (g/cm$^3$)

temperature, percentage of blend and the chemical structure have been generally used to calculate these properties without measurements. Some studies reporting these equations are summarized as follows. Tat and Gerpen [21] carried out a study about determination of specific gravities of soybean oil biodiesel and its blends with No. 1 and No. 2 diesel fuels at 75, 50 and 20% by weight from onset of crystallization temperature to 100 °C. According to experimental results, linear type relationship was found between specific gravity and temperature of biodiesel–diesel fuels blends. Therefore, the straight line correlation was well fitted to the experimental data and the lowest regression coefficient ($R^2$) was computed as 0.9989. Alptekin and Canakci [15] measured densities and kinematic viscosities of biodiesels derived from six different vegetable oils and its blends with two different diesel fuel (purchased from Shell Extra Diesel and Petrol Office firms). Linear and Arrhenius mixing equation were used to predict the densities and viscosities of the blends, respectively. In the study performed by Benjumea et al. [22] some basic properties (viscosity, density, heating value, cloud point temperature, calculated cetane index and T10, T50 and T90 distillation temperatures) of several palm oil biodiesel–diesel fuel blends were measured. In order to predict values of these properties, Kay and Arrhenius equations were evaluated as a function of the volume fraction of biodiesel. According to the absolute average deviation values (AAD), it was found that simple Arrhenius equations were suitable for predicting the basic properties. Tate et al. [23] obtained densities of three commercially available biodiesels at between from 20 to 300 °C by means of a capacitance type liquid level meter. According to results, densities were found to be linear behavior with temperature. Moreover, the linear regression coefficients ($R^2$) were obtained as 0.9911, 0.9872 and 0.9825 for canola methyl ester, soybean methyl ester and fish oil ethyl ester, respectively

The main objective of the present study is to investigate the effects of volumetric biodiesel percentage in blend (X) and temperature (T) on densities of produced corn oil biodiesel (B100) and its blends (B5, B10, B15, B20, B25, B50 and B75) with commercially available Ultra Force Euro diesel fuel (D) purchased from Shell. Some new one- and two-dimensional equations were fitted to the measurements and compared with other equations published in literature. Uncertainty analysis was performed to determine reliability of the measured density values. Moreover, in order to estimate flash point temperatures and higher heating values of these blends, some equations were evaluated as a function of biodiesel percentage in blend.

**Table 2**
Fatty acid methyl ester composition of the produced biodiesel.

| Fatty acid | Mass% |
|---|---|
| Palmitic (C16:0) | 15.190 |
| Oleic (C18:1) | 46.954 |
| Linoleic (C18:2) | 34.243 |
| α -Linolenic acid (C18:3) | 1.276 |
| Arachidic (C20:0) | 0.754 |
| Gadoleic acid (C20:1) | 0.657 |
| Behenic (C22:0) | 0.487 |
| Lignoceric (C24:0) | 0.439 |
| Average molecular mass | 292.870 g/mol[a] |
| Typical formula | $C_{18.77}H_{35.16}O_2$[a] |

[a] Calculated from fatty acid distribution.

## 2. Experimental methods

### 2.1. Biodiesel production

In this study, commercially available refined corn oil was used in biodiesel production. It was not needed to perform a pretreatment to the oil because of being refined. Thus, methanol ($CH_3OH$) of 99.80% purity as alcohol and pure grade sodium hydroxide (NaOH) as catalyst were used in transesterification reaction. In a master's thesis by Gülüm [24] and previous study by the authors [25], many reaction parameters, which influence the transesterification reaction, such as catalyst concentration, reaction temperature, reaction time and alcohol/oil molar ratio were varied within the range of 0.25–1.50%, 40–70 °C, 30–120 min and 3:1–12:1, respectively, and the effects of these parameters on changes of densities and, dynamic and kinematic viscosities of produced biodiesel were investigated parametrically to produce corn oil biodiesel having the lowest viscosity. Optimum reaction parameters were obtained as 0.90% catalyst concentration, 50 ° C reaction temperature, 60 minute reaction time and 9:1 alcohol/oil molar ratio [24,25]. Transesterification reaction was carried out in a 1 L flat-bottomed flask, equipped with a magnetic stirrer heater, thermometer and spiral reflux condenser. Isolab pycnometer and top loading balance with an accuracy of ± 0.01 g were used to measure density. Before starting the reaction, 1.80 g catalyst was dissolved in methanol in a narrow-neck flask to make alcoholic solution of catalyst. In the flat bottomed flask, this alcoholic solution was added to the 200 g corn oil that was formerly warmed to about 80 °C in a beaker. These reactants were mixed for 60 min at 50 °C with stirring speed of 500 rpm by means of the magnetic stirrer heater. Transesterification reaction was carried out with the spiral reflux condenser for avoiding loss of alcohol. Also, reaction temperature was controlled by using thermometer to remain at a constant temperature during the reaction. At the end of reaction, the resulting product mixture was transferred to a separating funnel. After a day, two phases occurred in the separating funnel. The upper phase consists of methyl esters (biodiesel) while the lower one consists of glycerol, excess methanol and the remaining catalyst together with soap. After separation of the two layers by gravity, the upper layer (biodiesel) was washed with warm distilled water until the water

**Table 1**
Some fuel specifications of diesel fuel, produced biodiesel and their blends, and corresponding standard values for biodiesel.

| Properties | Unit | D | B5 | B10 | B15 | B20 | B25 | B50 | B75 | B100 | EN14214 | ASTM-D6751 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Density at 15 ° C | kg/m$^3$ | 832.62 | 834.25 | 836.89 | 838.72 | 841.37 | 844.45 | 855.62 | 865.99 | 876.37 | 860–900 | [a] |
| Flash Point | ° C | 63 | 68 | 69 | 70 | 72 | 75 | 99 | 120 | 169 | 101 ≤ | 130 ≤ |
| HHV | kJ/kg | 45,950 | 45,368 | 44,984 | 44,643 | 44,399 | 44,205 | 42,700 | 41,310 | 39,930 | [a] | [a] |

[a] Not specified.

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