Key fuel properties and engine performances of diesel-ethanol blends, using tetrahydrofuran as surfactant additive

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Abstract. In this paper there were presented researches related to preparation and characterization of physicochemical properties of diesel-ethanol blends stabilized with tetrahydrofuran as surfactant, in order to be used as fuels in compression ignition engines. The main spray characteristics and engine performances of these blends were evaluated by using AVL Fire software. In the first stage of the studies, commercial diesel was mixed with ethanol, in different concentrations (between 2% and 15% v/v), followed by the addition of tetrahydrofuran (THF) until the blends were miscible, i.e. the blends were stabilized. The experiments were done at room temperature (22 °C). The obtained blends were characterized in order to determine the chemical composition and physicochemical properties, i.e. density, kinematic viscosity, surface tension. UV-Vis spectroscopy was utilized in order to determine a semi-quantitative evaluation regarding the chemical composition of the prepared blends and chemical interaction between diesel, ethanol and THF. Based on the determined properties, the fuel spray characteristics, engine performances and emission characteristics were evaluated by simulation using the AVL Fire software. The obtained results regarding physicochemical properties of blends were compared with diesel. Some improvements were observed when operating with the prepared blends compared to diesel with respect to engine performances and emission characteristics. Based on physicochemical evaluation and computer simulation, it was demonstrated that diesel-ethanol-tetrahydrofuran blends can be used as alternative fuel in compression ignition engines.

1. Introduction

Diesel fuel is used in internal combustion engines in many fields which include: automotive, engineering machinery, marine propulsion [1]. The consumption of fossil fuels leads to various types of air pollutants including nitrogen oxides (NOₓ), particulate matter (PM), carbon monoxide (CO) and other harmful substances. Moreover, around 60% of greenhouse gas emissions such as carbon dioxide (CO₂) are derived from the direct combustion of fuels [1,2]. Therefore, arises the need to replace part of the diesel fuel used currently with other alternatives. One of these alternatives is ethanol which can be manufactured from bio/renewable materials and by a process that would make it bio-ethanol. This compound can be made from many raw materials such as: sugar cane, molasses, waste biomass materials, corn, barley, sugar beets, cellulose [2,3,4]. Ethanol has been used before especially in combination with gasoline, but it has been tested with diesel fuel also and the blends obtained were technically acceptable for compression ignition engines [3,4,5].
In order to test the feasibility of using the diesel-ethanol blends in compression ignition engines it is important to compare the physical properties of the blends and to see if they are comparable and within standards that allow them to be used in these engines. Such properties include, but are not limited to: stability, density, viscosity, lubricity, flash point, safety [4]. These properties vary with the quality of the components used, for example the water content of the ethanol or the aromatic compound content of the diesel fuel [2]. Therefore it is important to describe the substances used because the results are only available for these specific concentrations.

Studies have shown that diesel-ethanol blends, that contain no more than 15% (v/v) ethanol, are a solution to reduce the quantity of fossil-fuel used by internal combustion engines, and these blends show acceptable properties that fulfill the standards required for diesel fuel. They are stable at medium temperatures, but for lower temperatures, in order to maintain the stability, additives need to be added [1,3,4,6]. The majority of these additives are surfactants that help reduce the surface tension between the two substances, making them more miscible. Surfactants that have been used before by other researchers include: biodiesel, stearyl alcohol (saturated), 1-hexanol, oleyl alcohol (unsaturated), methyl oleate (unsaturated with ester group) [1,3,7]. In order to improve the effectiveness of these substances some additional additives can be added. Due to their role and the quantity in which they are added, this being lower compared to the surfactants, they are called co-surfactants. Some of these are: 1-butanol, 1-octanol, 1-decanol [7].

2. Materials and methods

2.1. Preparation of alternative fuel blends
In order to prepare the diesel-ethanol blends, commercial winter grade diesel fuel, without biodiesel content, was supplied by Petrom (Cluj-Napoca, Romania) which presents the qualitative parameters required by European Standard EN 590. Ethanol (99.2% purity, water content: max. 0.8%) and tetrahydrofuran (99.5% purity, water content: max. 0.05%) reagents were supplied by Nordic Invest.

In the first stage of the studies, five diesel-ethanol blends were prepared by mixing ethanol (EtOH) with diesel in proportion between 2%(v/v) and 15% (v/v), under magnetic stirring condition (table 2). After the binary blends were prepared, tetrahydrofuran (THF) was added as surfactant, in order to obtain stability at room temperature (22 °C), i.e. diesel to become miscible with ethanol.

2.2. Physicochemical characterization of blends
Density and kinematic viscosity of diesel-ethanol stabilized with tetrahydrofuran blends were measured using an automated SVM 3000 Anton Paar rotational Stabinger viscometer, equipped with vibrating U-tube densimeter and Peltier elements to thermoregulate the sample. Surface tension was determined using stalgmometric method. In order to assess the hazard classification of prepared blends, flash point was measured using an automated Pensky Martens closed cup flash point analyzer HFP 339.

Semi-quantitative analysis for the determination of chemical composition and/or the interaction between components was made using UV-Vis spectroscopy and spectrofluorimetry (PL), respectively. UV–Vis absorption spectra of pure components and blends were taken on a JASCO V-550 spectrometer, in a wavelength range of 200–900 nm. Photoluminescence measurements were carried out using an Able &Jasco FP 6500 spectrofluorometer with a xenon lamp of 150 W as the excitation source and a photomultiplier tube (PMT) as detector. For comparison, all emission spectra were measured at room temperature with the same instrumental parameters using an excitation at 389 nm specific to diesel and emission originated from the luminescent centres at 423 nm. All spectra were registered exactly in the same conditions: excitation/reflection into 3 mL of liquid sample with identical incidence intensity, the excitation slit (3 mm) and emission slit (5 mm).
2.3. \textit{AVL Fire simulation procedure}

The model for engine simulation was developed in the AVL ESE Diesel simulation environment [8]. Based on the AVL 5402 type single cylinder engine, the main parameters of the model are presented in table 1. Since this engine has a symmetrical combustion chamber, only a 45° sector having a single injection hole was modelled (figure 1). The validation of the simulation model is described in detail in [9].

| Parameter | Value |
|-----------|-------|
| Bore x Stroke (mm x mm) | 90 x 85 |
| Compression ratio | 17.1 |
| Speed (min$^{-1}$) | 2500 |
| Number of holes, diameter and position ($-x$ mm $\times$ $^\circ$) | $8 \times 0.12 \times 162^\circ$ |

3. Results and discussion

3.1. \textit{Stability of prepared blends}

Room temperature stable blends were obtained by using tetrahydrofuran with concentration between 0.6\% (v/v) for diesel-2\% (v/v) ethanol blend and 7\% (v/v) for diesel-15\% (v/v) ethanol blend, respectively. The total volume proportions of blends were detailed in table 2.

| Sample | Diesel \% v/v | Ethanol \% v/v | Tetrahydrofuran \% v/v |
|--------|--------------|----------------|------------------------|
| Diesel | 100          | -              | -                      |
| 2\% EtOH | 97.4        | 2              | 0.6                    |
| 5\% EtOH | 92.7        | 4.9            | 2.4                    |
| 8\% EtOH | 87.6        | 7.6            | 4.8                    |
| 10\% EtOH | 84.8       | 9.4            | 5.8                    |
| 15\% EtOH | 79          | 14             | 7.0                    |
| EtOH   | -            | 100            | -                      |
| THF    | -            | -              | 100                   |
The stability of the blends was monitored for two months, until the prepared blends were considered homogenous. Therefore, in the first day of stability study, 1 mL THF was added into the 2% and 5% ethanol blends and 5 mL THF into the 8% to 15% ethanol blends and mixed using a magnetical stirrer, followed by keeping at room temperature for 3-4 days in order to observe if the phase’s separation has occurred. According with the observation it was noted that, after two weeks, by adding a total percent volume of 0.6% and 2.4% THF, respectively, the blends which contain 2% and 5% ethanol were stabilized. For blends which contain over 8% ethanol, stability has been achieved after two months, after total percent volume of 4.8%, 5.8% and 7% THF, respectively, was added. In figure 2, the ternary stability diagram of diesel-ethanol-tetrahydrofuran blends, at room temperature can be seen.

3.2. Physicochemical properties
Figure 3 depicts the variation of density with temperature, while figure 4 shows the density at 15 °C of diesel fuel, diesel-ethanol blends stabilized with THF, ethanol and THF pure components. It can be observed that for all the samples the density decreases linearly with temperature. Also, the blends’ density at 15 °C are smaller compared to diesel fuel (0.8416 g/cm³) which is attributed to the lower density of ethanol component, even if the density of THF is higher than superior limit for diesel density. However, the density at 15 °C of the blends are acceptable for the EN 590 standard; the inferior limit for diesel density is 0.8200 g/cm³. The obtained results are in accordance with the results presented by other researchers [10,11].
The kinematic viscosity measurements vs. temperature of pure components and blends are presented in figure 5 and it can be seen that THF presents small variations of viscosity with temperature, with a viscosity of around 0.62 mm²/s. Also, ethanol presents low kinematic viscosity with variations between 2.55 mm²/s at 0 °C and 0.92 mm²/s at 50 °C. According to the obtained data, blends which contained 2% and 5% ethanol (before adding THF) present a kinematic viscosity at 40 °C higher than the minimum level of viscosity for diesel fuel (2 mm²/s) which can be considered an acceptable limit for a standard diesel fuel (figure 6). However, the increase of ethanol concentration to 15% and the addition of the needed THF for stabilization, leads to a decrease of viscosity, value which exceeds the required minimum for diesel fuel. A low viscosity could cause more fuel pump leakage that would limit the amount of fuel delivered during high load conditions. A lower viscosity would also cause the pulverized fuel droplets to have a smaller dimension which would lead, for the same amount of volume injected, to an increase of surface area of the fuel droplet which would influence the evaporation characteristics [3,4].

Surface tension of diesel fuel plays an important role in the fuel’s combustion, affecting its initial stage, i.e. fuel atomization and spray characteristics. In figure 7 it can be seen that the surface tension of diesel is specific to a winter grade diesel (0.0309 N/m). For small concentrations of ethanol it can be observed that the value of surface tension is close to that of the diesel fuel (0.0306 N/m), but by
increasing the ethanol concentration over 5%, the surface tension tends to decrease to 0.0279 N/m. However, the surface tension of the blends falls within the limits presented in the literature data [2,12].

![Surface tension graph](image)

**Figure 7.** Surface tension at 20 °C of pure components and blends.

![Flash point graph](image)

**Figure 8.** Flash point of diesel and blends which contains 2%, 5% and 8% ethanol.

Even if the density, viscosity and surface tension properties of blends which contain ethanol in concentrations lower that 8% have good characteristic for utilization as fuel in diesel engines, the safety properties need to be considered for shipping and storage classification and precautions should be taken in handling and transporting of the prepared blends. Therefore, figure 8 emphasizes that, due to the low flash point of both ethanol and tetrahydrofuran (i.e. 17 °C and -14 °C, respectively), the flash point of blends dramatically decrease even at low concentration of the components. As a result, the transportation, handling and storage of the blends require additional safety measures in order to avoid ignition and explosions. Flash point of diesel-ethanol blends was discussed by other researchers and our results are in accordance with the literature data [3,10,13].

Using UV-visible analysis it was observed that there are no chemical interactions between diesel and ethanol or tetrahydrofuran compounds due to the fact that, in the spectra, there are no new absorption bands, other than diesel characteristic absorption bands (figure 9).

![UV-Vis spectra graph](image)

**Figure 9.** UV-Vis spectra of diesel and blends; Insert: PL spectra of diesel and blends.

The absorption bands at 350 nm and 375 nm wavelengths and emission bands from 420 nm and 445 nm identified upon excitation at 389 nm (insert figure 9), respectively, can be attributed with...
polycyclic aromatic compounds [14,15] from diesel structure. However, in the emission spectra it can be observed that the band from 420 nm increases while the band from 445 nm decreases, respectively, with increasing of ethanol and THF concentrations. Due to complex chemical structure of diesel fuel which is predominant formed from non-polar n-alkanes and moderately polar aromatic hydrocarbons, while ethanol present an highly polar character thru hydroxyl group, aromatic structures from diesel may interact with polar hydroxyl group of the ethanol and form transient dipoles or London dispersion forces which are a kind of intermolecular forces weaker than the hydrogen bond, leading to a stable and miscible bend [16,17]. At high concentration of ethanol, THF acts as a surface-active agent, leading to the formation of micelles which consists of polar heads and non-polar tails, forming a bridge between diesel and ethanol leading to formation of a miscible phase [3,10].

3.3. Simulation results
The variations of cylinder pressures for all fuels are presented in figure 10. In the cases of the blends, the ignition delays slightly increased (from 0.2 °CA – 2% EtOH to 0.7°CA – 15% EtOH) because of the low cetane number of ethanol and THF. Due to the diminished caloric values of the blends, the maximum values of in-cylinder pressures decreased with the increase in ethanol and THF contents (between 0.5% – 2% EtOH and 1.2 % – 15% EtOH). Same trends were observed in cases of the in-cylinder temperatures (figure 11). Consequently, the engine power is mildly reduced.

![Figure 10. Cylinder pressure as a function of crank angle.](image1)

![Figure 11. Cylinder temperature as a function of crank angle.](image2)

Except for CO emissions which increased significantly, the engine operation with the blends yielded better emission parameters in comparison to the diesel operation, as it can be observed from the figures 12 to 15. Comparing with diesel emissions, at the final of simulation, a decrease of NO emissions between 9% and 10.4% was observed (figure 12), with the increase of ethanol concentration (for the blends which contain 2% and 15%), while soot presents a drastic decrease from 15.5% up to 44%, for the blends mentioned above (figure 13). Also, a small decrease of CO₂ emissions (figure 14) of the blends was observed (from 0.46% specific to the blends which contain 2% ethanol to 1.28% in case of the blend with 15% ethanol content). However, a significant increase in CO emissions can be observed for the blends (up to 14%) comparative with diesel CO emissions (figure 15).
These improvements can be explained by lower combustion temperatures and the intrinsic oxygen content of the studied blends, which contributes to improving the combustion process. The CO emissions increased because of the prolonged ignition delay which reduced the allowable combustion time.

4. Conclusions
The studies presented emphasised the possible utilization of diesel-ethanol blends as alternative fuel in internal combustion engines, in order to decrease both utilization of fossil fuels and engine emissions, respectively. The blends were prepared using ethanol between up to 15% v/v concentration and based on stability studies it was observed that at low concentration of ethanol (under 5% v/v), the blends were stabilized at 22°C using 2.4 % v/v THF, in two weeks while at high concentration of ethanol, diesel and ethanol become miscible and stable only by adding up to 7% v/v THF.

Based on physicochemical characterisation of the diesel-ethanol-THF blends it was observed that density values are within the EN 590 limits, while the kinematic viscosity values of the blends which contain up to 5% v/v ethanol are located near the inferior limit of the standard, but for the blends with above 5% v/v ethanol, the kinematic viscosity values are under the inferior limit. Surface tension values slightly decrease with the increase of the ethanol and THF concentration, but overall these three
parameters of the blends have good limit values for utilization as fuels in diesel engines. However, due to the low flash point of both ethanol and THF, the blends present a flash point lower than 25°C which will require additional safety measures. Also, using VU-Visible spectroscopy it was emphasized that there are no chemical interactions between diesel and ethanol or tetrahydrofuran compounds and THF acts as a surface-active agent, forming a bridge between diesel and ethanol leading to formation of a miscible phase.

The engine simulation shows that the engine operation with the blends yielded slightly lower in-cylinder pressures and temperatures, but better emission parameters in comparison to the diesel operation.

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