Miscibility Analysis of Ethanol-Diesel Blends with Additives: A Comprehensive Investigation

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ABSTRACT

Diesel-Ethanol (DE) blends have gained attention as an alternative fuel due to their potential to reduce emissions and improve the performance of diesel engines. However, a significant challenge when dealing with DE blends is that of phase separation. Achieving optimal miscibility between ethanol and diesel often requires the addition of additives. This research article thoroughly examines the miscibility, blend stability, and phase separation of DE mixtures with various additives. To prepare blends for the miscibility analysis, DE blends with 10%, 15%, and 20% ethanol were mixed with selected additives (n-pentanol, n-butanol, ethyl acetate, and diethyl ether) at a 2% concentration in each blend. Prior to the miscibility analysis, all blends were mixed using a magnetic stirrer and a probe ultrasonicator. The results indicated that DE10 with 2% n-propanol, DE10 with 2% n-butanol, DE15 with 2% n-butanol, and DE10 with 2% diethyl ether exhibited good miscibility without phase separation or sedimentation after four weeks. However, it was noted that all the other blends with higher ethanol content were eventually phase-separated after four weeks.

Keywords-diesel; ethanol; additive; miscibility

I. INTRODUCTION

The diesel engine is an internal combustion engine that uses the compression ignition theory. Rudolf Diesel created it in the late 19th century, and it is currently utilized in a broad range of products, including cars, ships, trucks, generators and heavy machinery [1, 3]. Diesel is a liquid fuel generated with its producers having diesel engines in mind [4]. It is important to remember that the performance and emission characteristics of the diesel fuel in a diesel engine depend on engine design, control systems, fuel quality, and maintenance procedures. DE mixtures have been shown to maximize performance, reduce the emissions of diesel engines and are a very attractive solution when considering more environmentally friendly fuels [5]. However, ethanol displays low solubility in diesel [6]. The phase separation of DE mixtures is a problem that has been studied extensively and various solutions have been proposed. For example, authors in [7] studied the miscibility of ethanol in diesel and identified some miscibility issues. Diesel fuels with 5% ethanol were chosen to avoid cold flow problems and immiscibility problems with ethanol when water contact was prevented. Authors in [8] studied various fuel mixes, including pure diesel, diesel with methyl soyate, and diesel ethanol and methyl soyate. After being exposed to air for at least three months, the fuels with the additives maintained a high level of stability. In [9], plain DE mixtures and mixtures with 5% n-butanol as an additive for increasing solubility were tested. DE mixtures without n-butanol were not stable and phase separation occurred after 5 min for mixtures with 30% ethanol and after 72 h for the mixtures with 10% ethanol. However, the DE mixtures with 5% n-butanol exhibited higher stability and the phase separation was delayed for 11 days for the high concentration ethanol mixtures, while no phase separation was

observed for the mixture with 10% ethanol. In a similar study [10], the fuel instability and phase separation of ethanol/diesel blends were investigated. The ethanol solubility was influenced by water content and temperature. Since ethanol has low solubility in diesel, either a cosolvent such as n-butanol or an emulsifier such as Span 85 was used to avoid phase separation. The ethanol deployed in that study was 99.7% pure and the maximum ethanol content in the blends was less than 12.5%. A systematic study of the effect of different alcohols on the solubility of hydrous ethanol and diesel revealed that alcohols with a higher carbon number increased the miscibility of the blend, but the n-dodecanol resulted in the gelling of the DE blend. The n-hexanol and n-octanol were found to be the best cosolvent additives for the DE system due to acceptable fuel properties and phase stability [11]. In [12], DE was blended with 20%, 15%, 10%, and 5% ethanol separated after 2, 5, 24, and 80 hours, respectively. However, adding biodiesel to the mixture resulted in better stability, while phase separation occurred after 1, 3, and 9 days for 20%, 15%, and 10% ethanol concentrations, respectively. The addition of biodiesel to improve DE stability was also demonstrated in [13, 14]. In [15], methyl esters were added to diesel blends with ethanol or butanol. The stability of the blends regarding phase separation was tested at 10 ℃. The results revealed that 15% of the methyl esters can prevent phase separation in all DE mixtures. Nevertheless, higher amounts of methyl esters resulted in solid phase separation. The diesel-butanol fuels were stable regardless of the amount of methyl esters and butanol in the blend. Other additives that were proven to stabilize the DE mixtures were the surfactant cetyltrimethylammonium bromide [16], Nickel Zinc Iron Oxide ($NiZnFe_2O_4$) nanoparticles [17], and castor oil [18].

From the above literature review, it is evident that DE mixtures prepared only with stirring are unstable and phase separation will occur after a few hours or days for high or low ethanol content, accordingly. Therefore, it is essential to study thoroughly the miscibility of the mixture and find ways to increase the stability of DE blend. The main objective of this research work is to identify a suitable additive among the selected solvents (n-propanol, diethyl ether, ethyl acetate, and n-butanol) to increase the stability of DE mixtures and observe their effect on miscibility.

II. METHODOLOGY

The DE mixtures for the miscibility analysis were first prepared using a magnetic stirrer and then a probe ultrasonicator to increase miscibility, as evidenced in Figure 1. This two-step method ensures that the ingredients are well mixed and makes the mixture more stable for a longer time. The mixture was first stirred with a magnetic stirrer at 2500 rpm. The swirling motion of the magnetic stirrer produces a vortex that makes preliminary mixing possible. The mixture was then transferred to a probe ultrasonicator for its homogeneity to be improved.

III. EXPERIMENTAL PART

200 ml of the DE mixtures were prepared with different diesel-ethanol ratios. Thus, mixtures, namely DE10 (90% diesel + 10% ethanol), DE15 (85% diesel + 15% ethanol), and DE20 (80% diesel + 20% ethanol) were prepared and tested for miscibility stability. The physicochemical properties of diesel, ethanol, and of the mixtures are provided in Table I.

(a) (b)

Fig. 1. Equipment used for mixing the DE mixtures: (a) Magnetic stirrer and (b) probe ultrasonicator.

TABLE I. PHYSICOCHEMICAL PROPERTIES OF DIESEL, ETHANOL, AND DE MIXTURES

Property	Diesel	Ethanol	DE10	DE15	DE20
Density (kg/m^3)	824	790	821	819	817
Viscosity (mm^2/s)	2.95	1.15	2.77	2.68	2.58
Calorific value (kJ/kg)	43400	27900	41800	41000	40300
Cetane index	50	7	45	43	41
Flash point (°C)	40	12	37	35	34
Boiling Point (°C)	248.75	78.40	231.70	223.20	214.10

The mixtures showed poor stability and phase separation occurred after four weeks for the samples DE10, DE15 and DE20, as observed in Figure 2.

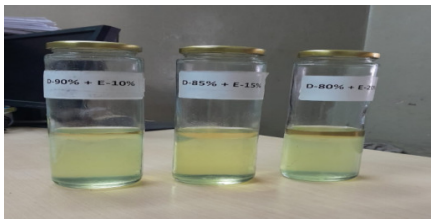


Fig. 2. Blends after four weeks.

Different additives can be employed to increase the compatibility of the DE blend. In this work, four additives, n-pentanol, n-butanol, ethyl acetate, and diethyl ether, purchased from Ajanta Chemicals, Ahmedabad, were tested for increasing the stability of the mixture and inhibiting the phase separation.

(a) (b)

Fig. 3. Experiment work on the magnetic stirrer and probe ultarsonicator.

2% additives were utilized in the DE10, DE15, and DE20 mixtures and their miscibility was observed after a few weeks. The initial mixtures were prepared in a glass flask and then stirred and ultrasonicated, as described in the Methodology section. The preparation of the blend and the results of this enhanced mixing can be noticed in Figure 3. Tables II-V illustrate all the DE blends after magnetic stirring, probe ultrasonicating, and the blend after four weeks for each additive. It is also noted whether phase separation was observed after four weeks.

TABLE II. 2% n-PROPANOL ADDITION IN BLENDS DE10, DE15, AND DE20

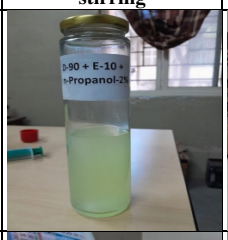
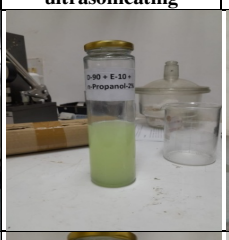
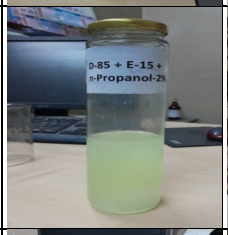
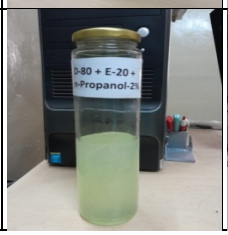
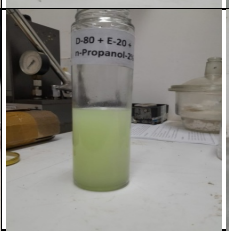
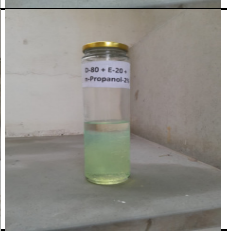
Sample	Blend after magnetic stirring	Blend after probe ultrasonicating	Blend after four weeks	Phase separation after four weeks
DE10 + 2% n-Propanol				No
DE15 + 2% n-Propanol				Yes
DE20 + 2% n-Propanol				Yes

TABLE III. 2% n-BUTANOL AS AN ADDITIVE IN BLENDS DE10, DE15, AND DE20

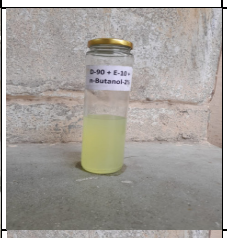
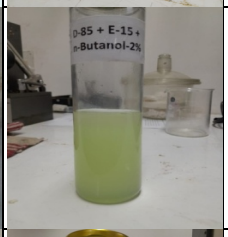
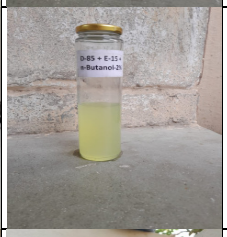
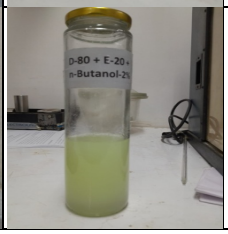
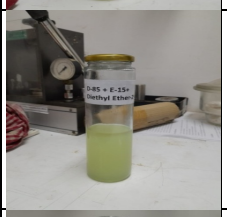
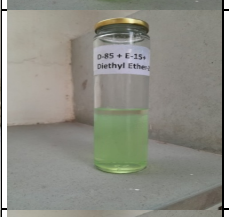
Sample	Blend after magnetic stirring	Blend after probe ultrasonicating	Blend after four weeks	Phase separation after four weeks
DE10 + 2% n-butanol				No
DE15 + 2% n-butanol				No
DE20 + 2% n-butanol				Yes

TABLE IV. 2% ETHYL ACETATE AS AN ADDITIVE IN BLENDS DE10, DE15, AND DE20

Sample	Blend after magnetic stirring	Blend after probe ultrasonicating	Blend after four weeks	Phase separation after four weeks
DE10 + 2% ethyl acetate				Yes
DE15 + 2% ethyl acetate				Yes
DE20 + 2% ethyl acetate				Yes

TABLE V. 2% DIETHYL ETHER AS AN ADDITIVE IN BLENDS DE10, DE15, AND DE20

Sample	Blend after magnetic stirring	Blend after probe ultrasonicating	Blend after four weeks	Phase separation after four weeks
DE10 + 2% diethyl ether				No
DE15 + 2% diethyl ether				Yes
DE20 + 2% diethyl ether				Yes

IV. RESULTS & DISCUSSION

Immediately after the preparation of the DE mixtures with the additives, all the mixtures appeared to be visually homogeneous, which indicates a good initial miscibility. No visible signs of phase separation or sedimentation were observed, suggesting that the DE mixtures with the additives were initially compatible. The mixtures were stored in a glass bottle, and after a four-week storage period, the blends were reexamined for any changes in miscibility. The following observations were made:

- The DE10 blend with 2% n-Pentanol showed good stability with no visible signs of phase separation or sedimentation, even after a storage period of four weeks. DE15 and DE20 mixtures with 2% n-pentanol demonstrated that phase separation occurred in the blend after four weeks.

- The DE10 and DE15 mixtures with the n-butanol additive exhibited good miscibility and no phase separation or sedimentation after four weeks, indicating stable blends. However, the DE20 mixture with 2% n-butanol displayed phase seperation after four weeks
- Regarding the ethyl acetate additive, all the mixtures (DE10, DE15, and DE20) with 2% ethyl acetate exhibited low stability, while phase separation occurred after four weeks.
- After four weeks, the DE10 with 2% diethyl ether mixture remained completely miscible, indicating stable blends with no visible signs of phase separation. On the contrary, DE15 and DE20 with 2% diethyl ether blends showed phase separation after four weeks.
- All DE20 samples exhibited phase separation after four weeks.
- The only stable DE15 mixture was that with n-butanol.

V. CONCLUSIONS

Diesel-Ethanol (DE) blends have emerged as a promising alternative fuel to reduce emissions and maintain the world's environmental sustainability. However, a significant challenge with DE blends is phase separation. Extensive research has been conducted to address this issue. In the present study, a miscibility analysis of DE blends with varying diesel/ethanol ratios was carried out. Mixtures of 90% diesel-10% ethanol (DE10), 85% diesel-15% ethanol (DE15), and 80% diesel-20% ethanol (DE20) were initially prepared using only a magnetic stirrer and a probe ultrasonicator. Phase separation was observed in all DE10, DE15, and DE20 blends. To enhance the stability of the mixtures and reduce phase separation, various additives were incorporated into the DE mixtures. New blends were prepared by adding 2% concentrations of n-pentanol, n-butanol, ethyl acetate, and diethyl ether to improve miscibility. All blends were mixed utilizing a magnetic stirrer and then a probe ultrasonicator before the miscibility analysis. The results indicated that DE10 with 2% n-propanol, DE10 and DE15 with 2% n-butanol, and DE10 with 2% diethyl ether exhibited good miscibility, showing no phase separation or sedimentation after four weeks. However, it was observed that all DE20 blends and DE mixtures with ethyl acetate were eventually phase-separated after the four-week period. N-butanol was identified as the most promising additive, as it produced the only stable DE15 mixture.

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