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Effects of Temperature and Storage on Stability of Bio-fuel Blends Prepared from Diesel, *Jatropha curcas L* oil and Ethanol (Anhydrous and Aqueous)

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ABSTRACT

The studies were conducted on stability and homogeneity of different blends of diesel and anhydrous (200° proof) and aqueous (190°, 180°, and 170° proof) ethanol prepared. The blends of ethanol, Jatropha curcas L oil and diesel were prepared by mixing them in several proportions. The blends which did not show any sign of phase separation at the initial stage were kept for three months at 40°C, 35°C, 30°C, 25°C, 20°C, 15°C, 10°C, 5°C and 0°C temperature and their stability was noticed every week by observing the phase separation change in colour and homogeneity. Observation of this study after three months was that the hybrid fuel blends except the Jatropha curcus oil-anhydrous ethanol (85:15) may be used as a diesel engine fuel because their stability and viscosity found within the limit.

Key words: *Bio-fuel, stability, blends, storage, energy*.

INTRODUCTION

Bio-fuels like ethanol and bio-diesel being as environment friendly will help us to minimize the emission of greenhouse gasses. As per the Biennial Update Report submitted by India, the quantum of India's total green house gas (GHG) emissions (excluding LULUCF i.e. Land-use, Land-use, Change and Forestry) in 2010 was 2.136 billion tonnes Carbon dioxide equivalent (CO2eq). Energy sector was the prime contributor to emissions and with 71% of total emissions in 2010. Energy sector includes - electricity production, fuel combustion in industries, transport and fugitive emissions. Industrial processes and product use contributed 8%; agriculture and waste sectors contributed 18% and 3% respectively to the national GHG inventory. A reduction of emission intensity of GDP by about 12% between 2005 and 2010 has been achieved against our voluntary pledge to reduce the emission intensity of its GDP by 20–25 per cent by 2020, compared with the 2005 level (TOI, 28-03-2017).

International experience has demonstrated the advantages of ethanol and methanol as automotive fuel. Blends of alcohols and ethanol have been singled out as the most prospective alcohol fuel. In addition to ethanol, methanol has also been used as alternate fuel but ethanol is more popular because it is a biologically renewable resource and it can be easily produced by the fermentation. It is non-corrosive, non-toxic and has higher heat of combustion with less volatility and provides better water tolerance than methanol. Ethanol, among these, has proven a track record as an automobile fuel and generally it is used as octane enhancer and oxygenate. Further, oils from more 300 plant seed are recognised and can be the source of bio-diesel. Among them, *Jatropha curcus curcas L.* (Ratanjot) hitherto considered as a wild oilseed plant of the tropics is now being credited as a most promising bio-fuel crop. The oil from *Jatropha curcus curcas* is odourless and colourless when fresh, but becomes yellow on standing (Verma *et al*., 2015).

In India, renewable liquid fuels viz. biodiesel, ethanol etc. are gaining utmost popularity. Several researches has been conducted biodiesel taking into account the preparation of bio fuel blends, evaluation characteristics of fuels, performance studies of engine on fuel blends, stability of blends, etc. The stability of biodiesel is still needs more attention in research. The stability of biodiesel is degraded during storage. Several fuel instabilities such as oxidation, storage and thermal stability give rise to formation of undesirable substances in biodiesel and its blends beyond acceptable quantities as per specifications and when such fuel is used in engine, it impairs the engine performance due to fuel filter plugging, injector fouling, deposit formation in engine combustion chamber and various components of the fuel system. Auto oxidation of biodiesel can cause degradation of fuel quality by affecting the stability parameters and oxidation instability can led to the formation of oxidation products like aldehydes, alcohols, shorter chain carboxylic acids, insoluble, gum and sediment in the biodiesel. Similarly, thermal instability is also concerned with the increased rate of oxidation at higher temperature which in turn, increases the weight of oil and fat due to the formation of insoluble. However, the storage stability is the ability of liquid fuel to resist change in its physical and chemical characteristics brought about by its interaction with its environment and may be affected by interaction with contaminants, light, factors causing sediment formation, changes in color and other changes that reduce the clarity of the fuel (Jain and Sharma, 2010).

Considering the above stated facts the present study was, thus, conducted to check the effect of temperature and storage stability of different fuel blends.

MATERIAL AND METHODS

The experiments were carried out using high speed diesel marketed by Indian Oil Corporation in accordance with IS: 1460-1974 as reference fuel, *Jatropha curcas L.* (Ratanjot) seed oil and anhydrous and aqueous ethanol. By using different proportions of *Jatropha curcas L.* (Ratanjot) seed oil and ethanol (anhydrous and aqueous) various blends were prepared with the diesel. The anhydrous ethanol (200^0 proof), of Merck make, Germany was procured from the local market of Pantnagar (Uttrakhand) and ethanol proofs of 200^0, 190^0, 180^0 and 170^0 were prepared from the anhydrous ethanol by adding different amount such as 0%, 5%, 10% and 15% of distilled water, respectively. More than 42 blends were prepared manually using different proportions of diesel, Jatropha curcus L oil and ethanol (anhydrous and aqueous) (190^0, 180^0, 170^0) and kept at ambient temperature for 24 h from the time of preparation. Further, to study the effect of various temperatures (0°C, 5°C, 10°C, 15°C, 20°C, 25°C, 30°C, 35°C, 40°C and 45°C) on stability of fuel blend, all blends were kept again for a period of 12 h in a Saveer Biotech make walk-in temperature control chamber designed to operate in 0-50°C temperature range. Initially the temperature control chamber was set at 45°C and the samples were kept for 12 h at that temperature to observe stability by visual inspection. After this, the temperature of control chamber was maintained at 40°C, 35°C, 30°C, 25°C, 20°C, 15°C, 10°C, 5°C and 0°C and the samples were placed at each of these temperatures for 12 h to observe phase separation. Nine samples (Table 1), thus, were sorted out for storage stability study on the basis of higher stability.

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Table 1. Fuel type codes and levels of independent parameters selected for engine test

S.No.	Ratio of independent parameters	Codes
1	Jatropha curcus L oil	F_J
2	Diesel (100)	F_D
3	Diesel-Anhydrous ethanol blends (75:25)	F_1
4	Diesel-Jatropha curcus L oil Blends (90:10)	F_2
5	Diesel-Jatropha curcus L oil Blends (80:20)	F_3
6	Diesel-Jatropha curcus L oil Blends (70:30)	F_4
7	Diesel-Jatropha curcus L oil- Anhydrous Ethanol Blend (70:20:10)	F_5
8	Diesel-Jatropha curcus L oil- Anhydrous Ethanol Blend (60:30:10)	F_6
9	Diesel-Jatropha curcus L oil- Anhydrous Ethanol Blend (50:40:10)	F_7
10	Diesel-Jatropha curcus L oil- Anhydrous Ethanol Blend (40:40:20)	F_8
11	Jatropha curcus L oil- Anhydrous Ethanol Blend (85:15)	F_9

Table 2 presents the fuel properties of all nine samples such as relative density and API gravity, kinematic viscosity, gross heat of combustion (ghc), cloud and pour point, flash point and fire point, ash content and carbon residue, acid value evaluated in accordance with BIS: 1448 [P: 32]:1992, Nakra and Chaudhary (1985), BIS: 1448 [P: 10]: 1984, IS: 1448 [P: 10]: 1970, IS: 1448 [P: 21]: 1992, ASTM D482-IP4, ASTM D189–IP13, London, ASTM D974–IP 1/64 of Institute of Petroleum, London (Verma et al., 2015). The stability or instability of blends was classified on the basis of visual observation. A stable blend is a clear, homogeneous and transparent solution with no sign of phase separation whereas an unstable blend looks turbid, non-homogeneous and opaque right since the time of formation. These characteristics of the blend do not change even after keeping them for a long period of time.

Table 2. Properties of different blends formulated with diesel, *Jatropha curucus* oil and anhydrous ethanol (Verma et al.2015)

S. No.	Blend [Diesel: Jatropha oil: Ethanol (anhyd.)]	Relative density (kg.cm^{-3})	API gravity	Kinematic viscosity (cSt)	Gross heat of combus - tion (MJ.kg^{-1})	Cloud point (^{0}C)	Pour point (^{0}C)	Flash point (^{0}C)	Fire point (^{0}C)	Carbon residue (%)	Ash content (%)	Total acidity (mg KOH.g^{-1})
1.	0:100:0 (F_J)	0.918	22.54	31.15	42.8	1	-6.5	236.0	251.5	4.850	0.165	2.24
2.	100:0:0 (F_D)	0.838	38.74	3.07	44.9	5	-1.3	58.0	64.5	0.142	0.0009	0.23
3.	75:0:25 (F_1)	0.829	37.78	2.51	47.91	4	3.0	35.0	41.0	0.101	0.0035	0.43
4.	90:10:0 (F_2)	0.855	34.75	3.66	49.16	3	-1.8	58.5	64.7	0.1086	0.0052	0.47
5.	80:20:0 (F_3)	0.860	32.92	4.30	48.34	2	-3.4	59.5	65.5	1.998	0.0096	0.77
6.	70:30:0 (F_4)	0.879	31.33	5.77	47.33	1.3	-5.0	60.0	67.5	2.332	0.0120	0.89
7.	70:20:10 (F_5)	0.848	37.44	3.90	45.94	1.8	-3.5	44.0	50.0	0.732	0.0033	0.51
8.	60:30:10 (F_6)	0.861	34.75	4.94	44.27	1.3	-3.5	46.0	54.0	1.449	0.0090	1.29
9.	50:40:10 (F_7)	0.869	33.21	5.25	43.66	1.4	-4.5	48.0	56.0	1.901	0.0105	1.70
10.	40:40:20 (F_8)	0.876	31.82	6.26	42.42	1.0	-6.8	49.0	56.5	2.987	0.0140	2.05
11.	0:85:15 (F_9)	0.884	28.45	15.2	44.47	4.5	-8.3	50.0	57.5	3.976	0.0195	2.08

RESULTS AND DISCUSSION

The past research in the area of ethanol use in C.I. engines indicates that majority of work has been done using anhydrous ethanol (200° proof). However, the commercial grade ethanol available has different levels of water content i.e. has different proofs. Ethanol proofs of 190°, 180°, and 170° were prepared from anhydrous ethanol (200° proof) by adding appropriate amount of distilled water. This range of ethanol proofs was selected because the previous study has indicated that the lowest ethanol proof which can be blended with diesel without phase separation at room temperature (25°C) is 170° when a diesel-ethanol blend having 15 percent ethanol by volume is prepared. Also, the diesel-ethanol blends prepared from 170° to 200° proof ethanol have shown similar power producing capabilities and increased brake thermal efficiency compared to diesel.

Effect of temperature on stability of fuel blends

The blends prepared using anhydrous ethanol and aqueous ethanol of 190°, 180° and 170° proof which were found stable at room temperature after 24 hours of preparation were tested further for stability under wide temperature range of 0, 5, 10, 15, 20, 25, 30, 35, 40 and 45°C. This stability test was conducted by placing the blends for 12 h at a selected temperature and observing phase separation by visual inspection. All blends were found clear and stable with no sign of phase separation in the temperature range of 25-45°C. At 20°C temperature except 200°-80-20 with sign of haziness and 200°-75-25, 200°-74-

26 and 200°-55-45 with partial phase separation all other blends were found stable and clear. It was also found that in the temperature range of 15-20°C the blends 200°-75-25, 200°-74-26, 200°-73-27, 200°-55-45, and 170°-60-40 have distinct phase separation.

However, all the other blends showed instability (distinct phase separation) in the temperature range 0-10°C. The stability of *Jatropha curcus* oil-ethanol blends under above said temperature range were found clear and stable with no sign of phase separation in the temperature range of 25-45°C. At 20°C temperature except 200°-80-20 and 200°-70-30 with sign of haziness and 200°-75-25, 200°- 74-26, 200°- 73-27 and 200°-55-45 with partial phase separation all other blends were found stable and clear. It was also noticed that in the temperature range of 15-20°C the blends 200°-80-20,200°-75-25, 200°-74-26, 200°-73-27 and 200°-55-45, were had distinct phase separation while all the other blends showed instability (distinct phase separation) in the temperature range 0-10°C. Thus, in order to achieve stability in large span of temperature (0-45°C) enhanced requirement of the blends was observed. A distinct phase separation was noted at the initial stage in the blends having Jatropha curcus oil mixed with 10, 15 and 20 percent aqueous ethanol of 190^0 proof. It is, therefore, seen that blending of aqueous ethanol (190^0 proof) with Jatropha curcus oil may not be feasible.

In contrast, this study recognized that blending of 10-15 percent anhydrous ethanol with Jatropha curcus oil appeared to be feasible. The blends when prepared using diesel and 10 to 90 percent Jatropha curcus oil indicated stability and had not shown any sign of phase separation.

Further, these blends were found to have a yellowish brown colour which was different from the colour of diesel and Jatropha curcus oil. It was also observed that the Jatropha curcus oil-diesel blends described above were thicker than diesel which was due to high viscosity of Jatropha curcus oil. Similarly, hybrid fuel blends were also prepared by using 40-70 % diesel, 5-55% Jatropha curcus oil and 5-25% anhydrous ethanol. Stable, homogeneous and soluble fuel blends with no sign of phase separation was found when 30 % diesel replaced with 10-25 percent Jatropha curcus oil and 5 to 20 percent anhydrous ethanol. The increase in content of anhydrous ethanol to 25 percent resulted in an unstable blend with distinct sign of phase separation. The stability of blends with 60 percent diesel was found only when Jatropha curcus oil and anhydrous ethanol blended in the range of 20-35% and 5-20%, respectively. Since, an unstable blend was formed when the level of anhydrous ethanol was increased to 25 percent. The blends containing 50 percent diesel, 30 to 45 percent Jatropha curcus oil and 5 to 20 percent anhydrous ethanol were also found to be stable with no sign of phase separation. It was also seen that stable blends replacing 55 percent diesel were obtained when 35 to 50 percent Jatropha curcus oil and 5 to 20 percent anhydrous ethanol were blended with diesel. The results also indicated that diesel replacement of 60 percent was obtainable from stable blends with no sign of phase separation when 40 to 55 percent Jatropha curcus oil and 5 to 20 percent anhydrous ethanol were mixed.

Therefore, from evident of the observations it can be concluded that in hybrid fuels, anhydrous ethanol may be blended up to 20 percent level because an increase to 25 percent level with possible diesel replacement between 30 to 60 percent resulted in the formation of unstable blends with distinct sign of phase separation.

Effect of temperature on stability during storage

The studies on phase separation and other characteristics indicate that anhydrous ethanol may be blended with diesel up to 20 percent level. The blending of 10 to 90 percent Jatropha curcus oil with diesel may also be possible. It was also seen that stability of diesel Jatropha curcus oil-anhydrous ethanol blends was limited by level of anhydrous ethanol which may preferably be kept between 5 to 20 percent. Thus, in order to study the effect of supplement larger quantity of diesel by anhydrous ethanol as well as Jatropha curcus oil, hybrid fuel blends as shown in Table 1 were selected. The blends shown in Table 1 and other fuel types were tested for long duration stability. The parameters viz. temperature stability, change in viscosity, were studied for a period of three months to assess the stability of blends with the passage of time. Temperature is most important parameter in determining the stability of the blends. Therefore, in order to assess the long duration stability of blends fuels in 0-45°C temperature range, the fuels were exposed to various temperatures (45°C, 40°C, 35°C, 30°C, 25°C, 20°C, 15°C, 10°C, 5°C and 0°C) during a period of three months.

Table 3 shows the details of observations on stability of blends during three-month duration. The observations on stability after one month revealed that only diesel-Jatropha curcus oil-anhydrous ethanol blends mixed in proportion (40:40:20) and Jatropha curcus oil-anhydrous ethanol blends mixed in the proportion of 85:15 in showed haziness in 0-5°C temperature range and all other blends were clear and transparent with no sign of phase separation in the temperature range 0-45°C. The observations on stability after two and three months indicate that only diesel-Jatropha curcus oil- anhydrous ethanol blends mixed in proportion (60:30:10), (50:40:10), (40:40:20) and Jatropha curcus oil-anhydrous ethanol blends mixed in the proportion of 85:15 showed haziness in 0-5°C temperature range, diesel- Jatropha curcus oil- anhydrous ethanol blends mixed in proportion (40:40:20) and Jatropha curcus oil-anhydrous ethanol blends mixed in the proportion of 85:15 showed haziness in 0-10°C temperature range and Jatropha curcus oil-anhydrous ethanol blends mixed in the proportion of 85:15 showed haziness in 0-20°C temperature range.

Table 3 Observed temperature stability of fuel types during three months period of storage

Selected fuel blends	Observations at various temperatures (°C)									
	45	40	35	30	25	20	15	10	5	0
At the time of preparation										
F_1	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_2	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_3	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_4	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_5	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_6	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_7	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_8	CS	CS	CS	CS	CS	CS	CS	CS	CS	H
F_9	CS	CS	CS	CS	CS	CS	CS	CS	CS	H
After one month of preparation										
F_1	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_2	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_3	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS

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F_4	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_5	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_6	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_7	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_8	CS	CS	CS	CS	CS	CS	CS	CS	H	H
F_9	CS	CS	CS	CS	CS	CS	CS	H	H	H
After two months of preparation										
F_1	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_2	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_3	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_4	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_5	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_6	CS	CS	CS	CS	CS	CS	CS	CS	H	H
F_7	CS	CS	CS	CS	CS	CS	CS	CS	H	H
F_8	CS	CS	CS	CS	CS	CS	CS	H	H	H
F_9	CS	CS	CS	CS	CS	CS	H	H	H	H
At three months of preparation										
F_1	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_2	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_3	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_4	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_5	CS	CS	CS	CS	CS	CS	CS	CS	CS	CS
F_6	CS	CS	CS	CS	CS	CS	CS	CS	H	H
F_7	CS	CS	CS	CS	CS	CS	CS	CS	H	H
F_8	CS	CS	CS	CS	CS	CS	CS	H	H	H
F_9	CS	CS	CS	CS	CS	H	H	H	H	H

Note: CS - Clear and stable with no sign of phase separation; H - Hazy with no sign of phase separation

However, these blends were found clear and stable when shaken. All the remaining blends were clear and stable after a period of two and three months. Thus, it was observed that all the nine blends fuels were stable under wide temperature range even after three months period.

Change in viscosity

It is well known that there is a limit for water contamination in ethanol-diesel blends in order to obtain stable blends. Ethanol, being highly hygroscopic in nature has high affinity to absorb water and may thus reduce the viscosity and hence stability of the fuel types in due course of time. Therefore, the change in viscosity of various fuel types was studied over a period of three months as shown in Table 4. It is evident from the table that the Jatropha curcus oil used in the experiment was having an initial kinematic viscosity of 31.15 cS which increased to 44.33 cS after a period of three months. This indicates a 42.31 percent increase in kinematic viscosity of Jatropha curcus oil used in the experiment after a period of 3 months. An increase in kinematic viscosity by 7 to 21 percent was observed for the selected diesel-Jatropha curcus oil blends after a period of three months.

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Table 4: Change in viscosity of selected fuels after three month of storage

Note: $\mathbf{F_J}$= Jatropha curcus L oil; $\mathbf{F_1}$= Diesel-Anhydrous ethanol (75:25); $\mathbf{F_2}$= Diesel-Jatropha curcus L oil (90:10); $\mathbf{F_3}$= Diesel-Jatropha curcus L oil (80:20); $\mathbf{F_4}$= Diesel-Jatropha oil (70:30); $\mathbf{F_5}$= Diesel-Jatropha oil-Anhydrous ethanol (70:20:10); $\mathbf{F_6}$= Diesel-Jatropha-Anhydrous ethanol (60:30:10); $\mathbf{F_7}$= Diesel-Jatropha oil- Anhydrous ethanol (50:40:10); $\mathbf{F_8}$= Diesel-Jatropha oil- Anhydrous ethanol (40:40:20) & $\mathbf{F_9}$= Jatropha oil- Anhydrous ethanol (85:15).

The change in kinematic viscosity of diesel-anhydrous ethanol mixed in 75:25 proportions was observed to be 18.32 percent. An increase in kinematic viscosity by 1.53, 7.89, 21.62 and 2.25 percent in blends of the diesel- Jatropha curcus oil - anhydrous ethanol mixed in 70:20:10, 60:30:10, 50:40:10 and 40:40:20 proportions respectively were also observed. The above observations, therefore, indicate that all the hybrid fuel blends except the Jatropha curcus oil-anhydrous ethanol (85:15) blend may be used as a diesel engine fuel even after a period of three months because their viscosity remained within the limit (2-7.5 cS) prescribed for diesel in IS : 1460 – 1974.

CONCLUSION

After two and three months only diesel-Jatropha curcus oil- anhydrous ethanol blends mixed in proportion (60:30:10), (50:40:10), (40:40:20) and Jatropha curcus oil-anhydrous ethanol blends mixed in the proportion of 85:15, diesel- Jatropha curcus oil- anhydrous ethanol blends mixed in proportion (40:40:20) and Jatropha curcus oil-anhydrous ethanol blends mixed in the proportion of 85:15 showed haziness in 0-10°C temperature range. In addition, jatropha curcus oil-anhydrous ethanol blends mixed in the proportion of 85:15 showed haziness in 0-20°C temperature range. However, these blends were found clear and stable when shaken. All the remaining blends were clear and stable after a period of two and three months. The hybrid fuel blends except the Jatropha curcus oil-anhydrous ethanol (85:15) were found stable and may be used as a diesel engine fuel even after a period of three months because their viscosity remained within the limit.

S. No.	Fuel Type blends	Kinematic viscosity (cS)		Percent increase (%)	Observations (Sign of phase separation)
		Initial	After 3 Months		
1	F_J	31.15	44.33	42.31	No sign of phase separation
2	F_1	2.51	2.97	18.31	No sign of phase separation
3	F_2	3.66	4.20	21.51	No sign of phase separation
4	F_3	4.30	5.23	21.62	No sign of phase separation
5	F_4	5.77	6.21	7.62	No sign of phase separation
6	F_5	3.90	3.96	1.53	No sign of phase separation
7	F_6	4.94	5.33	7.89	No sign of phase separation
8	F_7	5.25	6.42	21.62	No sign of phase separation
9	F_8	6.26	6.42	2.25	No sign of phase separation
10	F_9	15.2	20.11	32.30	No sign of phase separation

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