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Comprehensive Analysis for Developing Novel Fuel Blend by Ternary Analysis using Diesel – Canola Methyl Ester (Canol Biodiesel) – Ethanol; Liquid – Liquid Equilibrium

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Abstract— Biodiesel serves as the potential alternative for native fossil fuels. From previous researches it is found that straight biodiesel cannot be incorporated in engine, fuel modification is to be done to achieve the optimized performance and emission characteristics. Oxygenating the diesel has a significant impact on emission simultaneously it lacks the capacity to miscible with co-fuel in wide range of temperature for varying composition. In this research analysis, diesel-canola methyl ester- ethanol were blended at wide range of composition to obtain the novel fuel blend, 63 ternary blends and 3 binary blends were accumulated to develop the superior stable blend. Biodiesel is employed as substitute for amphipile, wide range of miscibility is observed, blends were observed for 168 hours and it found to be stable after 48 hours. 4 samples were selected from 2 regions for repeatability and 2 samples were picked with comparatively lower diesel percentage and optimal ethanol concentration. Inferences observed are as three layer, blurred double layer, double layer with one blurred layer, ring formation between layers and single blurred layer. Using biodiesel, activity of micelles were stabilized by preventing layer formation even at lower temperature of 27.2°C. Implementing ternary analysis for developing the optimal stable fuel blend possess the adequate advantage such as wide range of fuel miscibility, stable blend, storage at lower temperature, suitability for transportation, best fuel extender; whereas micro- emulsion of fuels disparagingly leads to increased aromatic emission and sudden impact on engine life due to presence of surfactant and co-surfactant. EN590 standards were followed to standardize the blends and properties were found to be in limits.

Index Terms—Amphipile, Biodiesel, Blend, Canola Methyl Ester, Co-surfactant, EN590, Ethanol, Ternary analysis, Micelles, Microemulsion, Oxygenate, surfactant.

1 Introduction

The increased susceptibility over crude oil resources, global crisis on petroleum products during 1970's urged to move through use-age of biofuel, E-Diesel (blends of ethanol in diesel) and gaseous fuel as a result of fuel crisis. Among the biofuels such as bio-diesel, ethanol, E-diesel were received significant attention to be used as alternative fuel in compression ignition engines [7, 11]. Biodiesel and diesohol comprises dramatic advantage over other fuels such as availability, domesticability, renewability, non-toxic, comparably low emission and employability. Biodiesel processed from various vegetable oils can be used as straight (B100) fuel or blended with diesel to incorporate in modern diesel engines. Instead Ethanol (E100), Ethanol in diesel blend is promoted as alternative fuel due to its improved physical properties such as cetane number, flash point and solubility than E100 [8]. E-diesel/Diesohol has the additional comprehensive property of fuel extender and oxygenator, Commonly Phase behaviour and layer separations were ad-jointly experienced while emulsifying ethanol and diesel, to overcome this various surfactants such as mono-oleates, alkanols and alkanolamides were commonly used, which has inverse effect on stability and performance. Incorporation of Fatty Acid Methyl Esters as amphiphile replacing the regular co-surfactants will prevent layer separation, controlled phase behaviour simultaneously improves viscosity, density and lubrication [15, 16]. On the other hand it reduces the complex steps of emulsification and act as co-solvent/surfactant thus making the more stable ternary blend. Proper utilization of ultrapure, anhydrous ethanol and biodiesel increases stability of ternary blend and performance of internal combustion engine.

Mufijur et.al [14] concluded that significant reduction in hydrocarbon, particulate matter and oxides of nitrogen can be achieved through blending biodiesel in diesel-alcohol mixture, which can be prominently used as alternative for petro-diesel fuel. Additionally they stated biodiesel concentration plays significant role in engine emission and ternary stability in their paper recent development on internal combustion engine performance and emissions fuelled with biodiesel-diesel-ethanol blends. Fernando et.al [5] in their paper development of a noval biofuel blend using ethanol-biodiesel-diesel microemulsion: EB-Diesel, developed binary and ternary phase diagrams to analyse the effect of sulphur content in different phases. Ultra Low Sulphur Diesel, Low Sulphur Diesel blends were taken and affirmated for further investigation. In the paper Feasibility

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of diesel-biodiesel-ethanol/bioethanol blend as existing CI engine fuel: An assessment of properties, methanol, material compatibility, safety and combustion by shahir et.al, [22] they investigated identification of low temperature stable blends and their properties were found to be with accordance to EN590. Blends suitable for cold climate were also profound significantly along with low sulphur content and highly oxygenates. Addition of iso-pentane overcomes the storage and transport problems. Ertan et.al [3] studied about use-age of palm oil biodiesel as an amphiphiles for diesohol emulsion. Inter-solubility of ternary fuel at low temperature and their physical characteristics were also discussed. Heat of combustion also analysed between ternary blend and conventional fuel.

The current research mainly focusses on implementing biodiesel (Canola oil methyl ester) as an amphiphile in stabilising E-diesel (ethanol in diesel blend). The phase stability and layer formation of biodiesel-diesel-ethanol ternary system if thoroughly investigated at different component concentration for prolonged period along with few basic characteristics of stable blend obtained from resultant.

2 Materials And Methods

Ternary analysis was carrier distinctly at various ratios (% v/v) of diesel [1, 18], bio-diesel and ethanol in constant temperature for extended period of time. To form the fuel blends, diesel was obtained from local commercial fuel pump station and anhydrous ethanol of 99.95% purity was purchased from proxor scientific & co, Chennai. Biodiesel (Canola oil methyl ester) was derived from canola oil which is extracted from dried, finely powdered canola seeds procured from local vendor of Rajasthan. Soxhlet Extraction Procedure is followed to extract oil from powdered seeds at optimised temperature range of 60°C to 75°C with n-hexane as extraction medium [10]. Further base catalysed transesterification in the presence of 2% KOH concentration to weight of oil, 1:5 molar ratio of methanol to oil is employed to derive the canola oil methyl ester at 50°C to 65°C of reaction temperature and reaction time of 60 to 90 minutes to achieve the conversion efficiency of 93.4%. Further 8 hours of settling period was allowed and glycerol sedimentation was removed by gravity separation method.

Spectroscopic studies such as 1H & 13C-NMR, GC-MS and FTIR were carried out in Bruker AVANCE III 500 MHZ multinuclei solution NMR spectrometer, PERKIN ELMER spectrum and FTIR , JOEL GC MATE II GC-MS. Investigations confirm the presence of various Fatty Acid Methyl Esters in biodiesel derived. The test summarizes presence of 9 fatty acid methyl esters such as Lauric acid, Myristic acid, Palmitoleic acid, Pentadecylic acid, Linoleic acid, Oleic acid, Arachidic acid, Gondoic acid, Behenic acid.

Investigations on solubility, phase behaviours, solubility and fuel properties of diesel-biodiesel-ethanol were done using ternary phase diagram. Ternary fuels were mixed into homogeneous mixture using magnetic stirrer for 120-180 seconds [17]. Resulting blend was kept in a glass tube as shown in fig. 1 & 2. Observations were made at every 24 hours, which reminded undisturbed at room temperature of 27.2ºC to find out the phase stability at low temperature environment. Blend mixtures varying from 0 to 100 % by volume of about 66 samples were taken for study.

Fig. 1. Ternary analysis - Top View

Ternary phase diagram (as shown in fig. 3) is used to clearly depict the phase behaviour and physical appearance. Table 1 shows the various ratios of blends that were made for ternary analysis.

Fig. 2. Ternary Analysis – Front View

3 Results And Discussion

3.1 Inferences of Ternary analysis

Ternary blends were made according to the boundary layer reference comprising Diesel-Biodiesel-Ethanol at each boundary side [20]. Blend is formed using Diesel-Ethanol initially, followed by biodiesel mixing in %V/V method. Gradual change in volume from 0 to 100% at the rate of 10%. Resulting ternary phase comprises 63 ternary blends and 3 binary blends. Observations were made at every 24 hours, resulting inferences viz single phase, single phase blur, two phase and three phase. Fig. 4 shows the different inferences observed at 24 hours of settling period.

TABLE 1
RATIOS OF DIESEL-BIODIESEL-ETHANOL IN % VOLUME FOR TERNARY ANALYSIS

Diesel – Biodiesel – Ethanol Ternary Analysis Ratios											
S.No	**Diesel**	**Biodiesel**	**Ethanol**	**S.No**	**Diesel**	**Biodiesel**	**Ethanol**	**S.No**	**Diesel**	**Biodiesel**	**Ethanol**
1	00	50	50	**23**	30	45	25	**45**	40	10	50
2	05	50	45	**24**	30	40	30	**46**	45	50	5
3	05	45	50	**25**	30	35	35	**47**	45	45	10
4	10	50	40	**26**	30	30	40	**48**	45	40	15
5	10	45	45	**27**	30	25	45	**49**	45	35	20
6	10	40	50	**28**	30	20	50	**50**	45	30	25
7	15	50	35	**29**	35	50	15	**51**	45	25	30
8	15	45	40	**30**	35	45	20	**52**	45	20	35
9	15	40	45	**31**	35	40	25	**53**	45	15	40
10	15	35	50	**32**	35	35	30	**54**	45	10	45
11	20	50	30	**33**	35	30	35	**55**	45	05	50
12	20	45	35	**34**	35	25	40	**56**	50	50	0
13	20	40	40	**35**	35	20	45	**57**	50	45	5
14	20	35	45	**36**	35	15	50	**58**	50	40	10
15	20	30	50	**37**	40	50	10	**59**	50	35	15
16	25	50	25	**38**	40	45	15	**60**	50	30	20
17	25	45	30	**39**	40	40	20	**61**	50	25	25
18	25	40	35	**40**	40	35	25	**62**	50	20	30
19	25	35	40	**41**	40	30	30	**63**	50	15	35
20	25	30	45	**42**	40	25	35	**64**	50	10	40
21	25	25	50	**43**	40	20	40	**65**	50	05	45
22	30	50	20	**44**	40	15	45	**66**	50	00	50

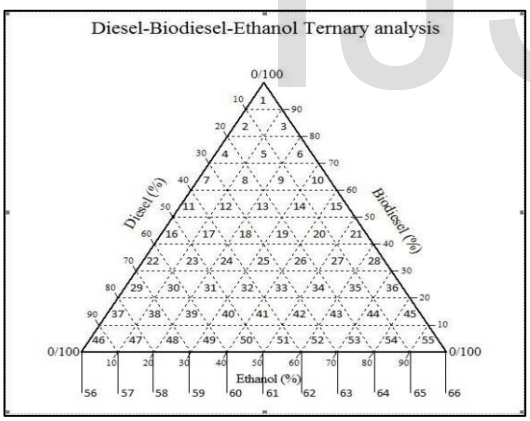

Fig. 3. Layout of Ternary analysis

Phase conversion happens after certain time interval i.e solubility of liquid in liquid takes place whereas miscibility of liquid is primary of ternary blend, samples showing layer separations were illustrated in table 2. Phase change and Stability of blend changes with different time period. Stable samples were identified at the end of 48 hours at three different regions [13, 23]. Random stable samples were taken from three different regions for further processing. Four samples (say sample number 3, 26, 39, 40) with high stability and relatively lower diesel percentage were taken for repetition, after three trials of each six days of observations. Two samples were randomly selected of high stable blend (say 26, 39) and distinguishingly higher biodiesel percentage.

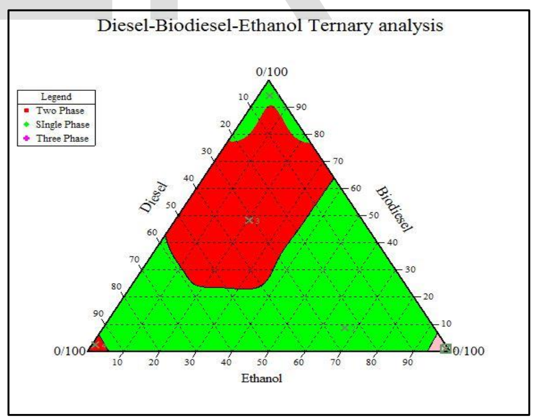

Fig. 4. Inferences of ternary analysis at 24 hours.

EN 590 standards were referred to compile the standards of canola biodiesel, sample number 26 and 39; since the fuel emulsification is done and found to be in limits, table 3 shows the comparison

TABLE 2
SAMPLE SHOWING LAYER FORMTIONS.

S.No	Diesel	Biodiesel	Ethanol	S.No	Diesel	Bio-diesel	Ethano
5	10	45	45	51	45	25	30
7	15	50	35	52	45	20	35
20	25	30	45	53	45	15	40
33	35	30	35	54	45	10	45
35	35	20	45	55	45	05	50
43	40	20	40	62	50	20	30
44	40	15	45	63	50	15	35
45	40	10	50	64	50	10	40
50	45	30	25	65	50	05	45

TABLE 3
PROPERTIES COMPARISON OF CANOLA BIODIESEL, SAMPLES 26 AND 39.

Properties	Limits (EN590 Standards)	Canola Biodiesel	Sample Number 26 (30-30-40)	Sample number 39 (40-40-20)
Cetane number	51 (Min)	61	54	58
Density	820 – 845 Kg/m3	838	824	832
Flash point	55°C (Min)	98	78	82
Oxidation Stability	25 g/m^3 (Max)	19	22	20
Viscosity	2.0 – 4.5 mm^2/s	4.4	3.1	3.8

3.2 Effect of Ethanol in Ternary Blend

In this ternary analysis 99.95% ultra-pure ethanol is employed to obtain the optimal miscibility results [12]. Presence of water content in ethanol above 0.05% results in poor inter-solubility and emulsion stability with diesel and biodiesel due to polar property at higher rate. On the other hand 99.95% pure ethanol is used in the ternary blend due to their higher oxygenate property of about 35% by its weight ratio and ability to mix at any ratio with diesel irrespective of temperature. Inferences previously obtained at 24 hours comparatively differs at 48 hours observation. Fig. 5 pictures inference at 48 hours and table 4 defines the standard single layer samples at all three different regions as observed.

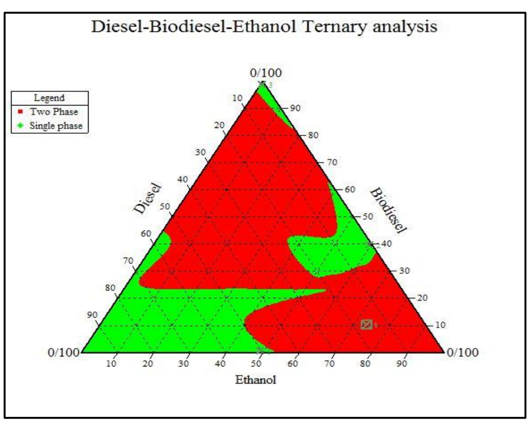

Fig. 5. Inferences of ternary analysis at 48 hours.

Even though presence of traces of water (0.05%) in ethanol causes layer separation with diesel due to absences of micelles (Polar head and Non-polar tail) [6, 9]. It is overcome by addition of biodiesel as amphipile, causing exchange of polar head to ethanol and tail to diesel thus resulting in stable single phase formation. The inverse proportional of ethanol to biodiesel at much different but better solubility of one liquid in another was observed. Here resulting stable ratios show the high miscibility of ternary liquids. Also ethanol has the significant effect on properties of samples selected as stable and improves the fuel property making it viable for unrestricted use-age.

3.3 Effect of Biodiesel in Ternary Blend

Distinctive characteristic of ternary blend is high miscibility and stability. Bio-diesel used to reduce the polar nature of ethanol thus acts as an amphipile to produce the stable blend by reducing the aromatic activity of ethanol, which leads to layer separation and phase formation between ethanol and diesel. Addition of biodiesel in the blend will reduce use-age of co-surfactants that causes significant adverse effect on performance [2, 4]. Added advantage of using bio-diesel as replacement of surfactants has the required effect of micelles causing no layer formation with single layer blend.

TABLE 4
SAMPLES SHOWING SINGLE STABLE LAYER AFTER 48 HOURS OF OBSERVATION.

S.No	Diesel	Biodiesel	Ethanol
1	00	50	50
3	05	45	50
15	20	30	50
21	25	25	50
22	30	50	20
26	30	30	40
27	30	25	45
28	30	20	50
29	35	50	15
34	35	25	40
36	35	15	50
37	40	50	10
38	40	45	15
39	40	40	20
40	40	35	25
41	40	30	30
42	40	25	35
46	45	50	5
47	45	45	10
48	45	40	15
49	45	35	20
57	50	45	5
58	50	40	10
59	50	35	15
60	50	30	20
61	50	25	25

4 CONCLUSION

Demonstration for use-age of biodiesel as amphipile for replacement of surfactant and co-surfactant is critically reviewed to fulfil the requirements to meet the diesel-biodiesel- ethanol blend implementation in commercial internal combustion engine [19, 21]. The following are the conclusions of study,

1. Stability of the fuel sample changes with time and disappearance of layer occurs.
2. Highly soluble, single layer and stable blends were undergone repeatability to confirm its physical stability.
3. Stable samples were found at three different regions and two samples with lower diesel percentage were taken respectively.
4. EN590 Standards were referred to check the density of the ternary blend and found to be in limits table 3.
5. Flash point, Fire point, cetane number and kinematic viscosities were found to meet the standard limits.
6. Addition of ethanol comparatively reduces the sulphur content than the commercial diesel.
7. Ternary blends obtained were water tolerance, possible for transportation and storage, viability at lower temperature is also checked.

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