Biodiesel-water emulsions: An alternative approach for conventional fuels

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ABSTRACT: - *Emulsified fuels have more priority in reducing nitrogen oxide and smoke simultaneously than as compared to conventional fuels. Present investigation describes the process to formulate highly stable water-in-Biodiesel emulsion, which gives minimum hazardous exhaust emission. For making emulsion, surfactant blends were screened for their effectiveness in stabilizing water in biodiesel emulsion system. The Biodiesel was mixed with water in different the ratios to investigate the stability & characteristic of fuel. Effective results were obtained with blend of SPAN 80/TWEEN 80. A high speed mixing homogenizer technique was used to obtain the resultant water in biodiesel emulsion containing blend of SPAN 80/TWEEN 80. It was observe that the emulsions stability decreases as water concentration increases.*

KEYWORDS: Water-in-Biodiesel emulsion, Stability, Surfactant, Mixing, Viscosity

INTRODUCTION

The emulsion fuel is an emulsion of water in fuel with specific additives & surfactants, to reduce the emissions of nitrogen oxides and particulate matters. Diesel engines are necessary but at the same time the reduction of non-renewable sources of energy and strict emission regulations drive us to search for alternative fuels. Several researchers have investigated the properties of a bio-diesel from vegetable oils in diesel engines and found that particulate matter (PM), CO, and soot emissions were decreased, while NOx emissions were increased [1-3]. Biodiesel is a promising substitute fuel which gives reasonably satisfactory performance, reduced emissions and does not require any engine modifications [15]. Emissions like NOx can be reduced either by retarding the injection timing or by including the exhaust gas recirculation (EGR) system [12]. Emulsified fuels are accorded more priority due to the simultaneous reduction of NOx and smoke. Water can be mixed with the fuel using various methods such as: injection into the intake air, direct injection into the cylinder, and emulsification with water. No engine modification is required to use the emulsified fuel directly in the cylinder [13]. Faster combustion reaction takes place in the water emulsified fuels due to the formation of micro-explosion phenomenon [5]. The combustion efficiency and the brake thermal efficiency (BTE) is improve by using water emulsified fuel and also reduce the formation of NOx, soot, HC, and particulate matter (PM) [14-15]. Rajan and Senthil Kumar 4 have studied the effect of exhaust gas recirculation on the performance and emission characteristics of a twin cylinder diesel engine with sunflower oil methyl ester. They studied that slight increase in CO and HC emission for 15% EGR at full load compared with diesel fuel but NOx and smoke emissions were decreased. Kandasamy and Marappan [5] have studied the performance of a diesel engine with Biodiesel with water emulsion in the ratios of 5%, 10%, 15% and 20% in a direct injection diesel engine. They studied that slight improvement in brake thermal efficiency accompanied by the drastic reduction in NOx emission. It is also found that 15% water emulsified fuel showed the best performance and less emission than the other combinations, Yasimoto and Tamaki [6-7].

The biofuel play as a key element for renewable and prevention energy scenario. Thus, biodiesel fuel has a potential for external combustion especially in burner combustion. However, biodiesel combustion still have problem of emitting NOx, CO and Particulate Matter (PM) into the atmosphere. For that reason, biodiesel-water emulsion is the simpler and cheapest way to reduce the emission of combustion. Therefore, the emulsification concept from biodiesel and water were studied with focusing in controlling of combustion process in order to minimize the harmful emission [8-10].

The main focus of this research is to formulate Water in Biodiesel fuel emulsion and to analyze physical properties of that fuel emulsion. We first determined the appropriate composition of biodiesel and water to make suitable fuel emulsion and then emulsification characteristics, fuel properties of the blends at different blending compositions were investigated. Further, effect of water & emulsifier on emulsion preparation, homogeneity, stability and physical properties was also analyzed.

MATERIALS AND METHODS

Materials:-Nonionic surfactants TWEEN 80, SPAN 80 and SPAN 85 were supplied by Unitop chemical Pvt. Ltd. and Croda India Pvt. Ltd., respectively. Distillated water was used for emulsion preparation. Methanol (99-100%), ethanol (99-100%), sodium hydroxide pellets (96%), potassium hydroxide pellets (>84%), phenolphthalein (PH 8.2-9.8), diethyl ether, hydrochloric acid (37%). All the chemicals were used as analytical reagent grade. Soybean oil was collected from local market.

Methods

Preparation of Biodiesel

Biodiesel was prepared in the laboratory via basic catalyst trans-esterification of Soybean oil with Methanol at 60^{0}C and atmospheric pressure. The glycerol enriched phase produced was removed by decantation and biodiesel enriched phase was washed several times with water. After washing, the biodiesel was heated up to 100^{0}C to remove any remaining water and alcohol. The technical characteristics of Biodiesel are mentioned in Table 1. All the chemicals used were of analytical grade confirming to the specifications

Preparation of Water in Biodiesel emulsion:-

Emulsions were prepared using a homogenizer emulsification device in two steps.

1. First Step: Blended surfactants (SPAN+TWEEN) were mixed into Biodiesel. Then, pre-emulsions were prepared by adding certain amounts of water into the mixture of surfactant and diesel fuel with constant stirring at 800 rpm.
2. Second Step: In the second step, the prepared pre-emulsions were stirred at high speed (5000 rpm) for 20 min. All emulsions were prepared at room temperature

Analysis of emulsifier

Surface tension measurements

Different molar concentrations of SPAN & TWEEN blends were used for surface tension measurement. Emulsifier mixture was dissolved in distilled water and their surface tensions were determined at 30^{o}C using De Nouy tensiometer ring "Kruss model Gmbh K100". The instrument was daily regulated with distilled water.

Critical micelle concentration

CMC of Blended SPAN and TWEEN (ST) was determined by the method adopted by Rosen [10]. The interfacial tension concentration isotherms (IFTC) curves were plotted for the prepared surfactants at different temperatures. The CMC values were determined from the abrupt change in the slope of the IFTC curves.

Surface excess concentration (Γmax)

Γ_{max} is a useful measure of the effectiveness of adsorption of surfactant at the liquid/air or liquid/liquid interface since it is the maximum value to which adsorption can be obtained. Γ_{max} can be calculated from Gibbs eq. (1).

$$\Gamma_{max} = -\left(\frac{1}{RT}\right)\left(\frac{\partial \gamma}{\partial \ln C}\right) \qquad (1)$$

Minimum surface area per molecule (Amin)

A_{min} is the minimum area per molecule (nm^2/molecule) at the oil-water interface. The average area occupied by each adsorbed molecule is given by Eq. 2.

$$A_{min} = \frac{10^{16}}{\Gamma_{max} . N_A} \qquad (2)$$

Where, N_A= Avogadro's number.

Effectiveness (πCMC)

The effectiveness of adsorption or surface pressure (π_{CMC}) of the surfactant was also calculated from the Eq. 3.

$$\pi_{CMC} = \gamma_o - \gamma_{CMC} \qquad (3)$$

Thermodynamic parameters of micellization

The ability of micellization process depends on thermodynamic parameter (standard free energy, ΔG_{mic}). The ΔG_{mic} was calculated by choosing the following expression Eq. 4.

$$\Delta G_{mic} = 2.3\ RT\ (1-\alpha).\ \mathrm{Log}\ (CMC) \qquad (4)$$

Thermodynamic parameters of adsorption

Many investigators dealt with the thermodynamics of surfactant adsorption at interface. The thermodynamic parameter values of adsorption ΔG_{ad} were calculated by using Eq. 5.

$$\Delta G_{ad} = \Delta G_{mic} - 0.623.\ \pi_{CMC}.\ A_{min} \qquad (5)$$

RESULTS AND DISCUSSION

Table1.Physicochemical characteristics of Biodiesel

Sr.no	Physical properties	Value
1	Density (Kg/m^3	860
2	Calorific value (*kJ/kg)*	41320
3	Acid value	0.32
4	Kinematic viscosity, at 40 ^{0}C (cst)	4.5
5	Flash point ^{o}C	170
6	Cloud Point ^{o}C	3
7	Water content wt.%	0.05
8	Cetane number	65
9	Copper corrosion	Class 1 max

Table 2. Analysis of the Blended emulsifier

Sr.no	Mix Surfactant	ST	IFT	Γ_{max}	A_{min}
1	SPAN 80: TWEEN 80	33	10.85	3.44	48.16

Table 3. Analysis of the Blended emulsifier

Sr.no	Mix Surfactant	Π_{CMC}	CMC	ΔGad	ΔG mic
1	SPAN 80: TWEEN 80	61.15	4.75	-18.96	-17.18

ST- Surface tension (mN/m); IFT- Interfacial Tension (mN/m); Γ_{max}- surface excess concentration; A_{min}- minimum surface area per molecule; Π_{CMC}- Effectiveness; CMC- Critical Micelle Concentration; ΔGad- Thermodynamic parameter of adsorption; ΔG_{mic}- Thermodynamic parameter of micellation

Effect of consumption of Blended surfactants, water content and HLB on water in biodiesel emulsion stability

Tween 80/Span 80 was used as the mixed surfactant system to make water-in-Biodiesel emulsion. The influence of the consumption of blended surfactants on the stability of water-in-biodiesel emulsion was investigated and the results were shown in Fig. 1 and 2. Generally, the stabilization time increased as the consumption of blended surfactants increased. It is cleared from figure 1 and 2 that the stabilization time was the highest for blended surfactant systems having HLB value of 9. The stabilization time of the emulsions using mixed Span 80/Tween 80 emulsifier went up to 4 days.

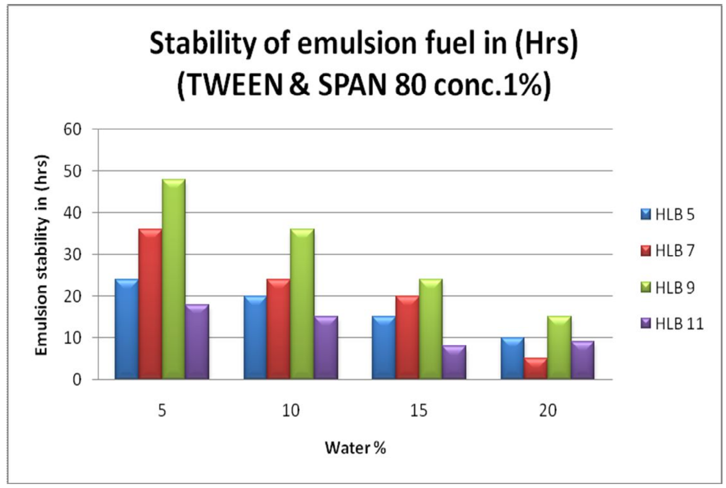

Figure 1. Stability of water in biodiesel emulsion (in hrs) at surfactant concentration 1%. (Mixing time= 20 min.; mixing speed= 5000 rpm).

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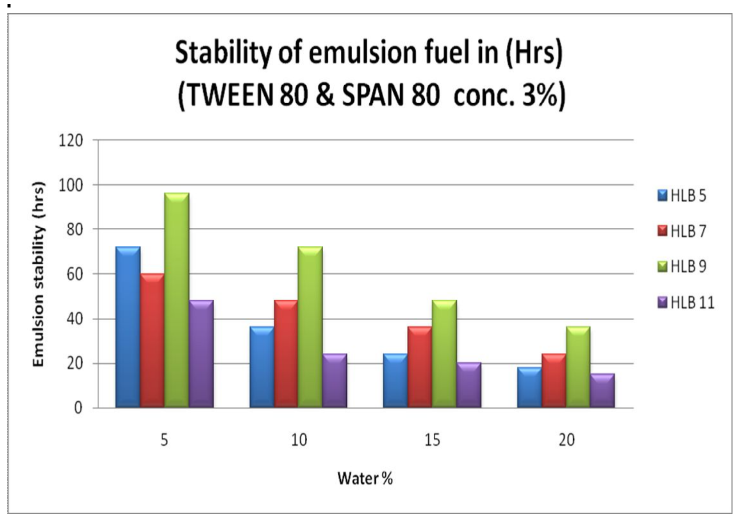

Figure 2. Stability of water in biodiesel emulsion (in hrs) at surfactant concentration 3%. (Mixing time= 20 min.; mixing speed= 5000 rpm).

Figure 1 and 2 shows that as the percentage of water increases, the stability of emulsion decreases. At 5% water in emulsion, the maximum stability was achieved for all concentrations of blended surfactants. The emulsion stability reached the lowest value beyond 15 % water concentration and remained almost stagnant beyond that point. The Water in biodiesel emulsion remained stable only for 4 days and then the water got separated.

The surfactant plays a very complicated but important role in emulsion stability. Effectiveness of the surfactant is determined by transportation of surfactant molecules to Water in biodiesel interface and get absorbed to form a surface layer. Figure 1 and 2 depict the effect of surfactant concentration on stability of W/Biodiesel emulsion. The emulsion stability found to be increased with increase in the surfactant concentration from 1% to 3%. The maximum stability observed at 5% W/Biodiesel emulsion with 3% surfactant concentration. The emulsion was stable for 4 days without any water separation. Therefore, even though 5 % W/biodiesel emulsion gives highest stability, we recommend 5% W/biodiesel emulsion at 3 % surfactant concentration.

FUEL CHARACTERIZATION

The various fuel properties namely density, viscosity, calorific value, flash point and Pour Point, copper corrosion, Cetane number of Water in biodiesel emulsified fuel were determined. Table 9 shows the properties of the studied fuels, From Table 9 it is observed that the increase in the flash point is mainly due to the presence of water. All fuels had density values higher than those of biodiesel and this value increased with water content. This was due to higher density of water as compared to biodiesel. The presence of surfactant improves interactions between the oil and water phases. As the water percentile increases, more complex micellar structures are formed, thus resulting in increased viscosity. Values above 6 cst can damage the fuel injection system, causing incomplete combustion and, consequently, more pollution by carbon monoxide and higher fuel consumption but in emulsified biodiesel it was found that the viscosity was well within the limits prescribed by the Indian standards for biodiesel. The calorific values of emulsified biodiesel, which were lower than that of waste cooking oil based biodiesel. This was due to increase in water content of emulsified fuel, calorific value decreased, because water present in the fuel was converted to steam by using some of the heat evolved by the combustion of fuel and the steam found during combustion was not condensed then this amount of heat was lost resulting in lower calorific value. The present of water content also effect on Cetane number of emulsified biodiesel. As the water content increases the Cetane value of fuel decreases but in emulsified biodiesel the Cetane number was found well within the limits prescribed by the Indian standards for biodiesel. The results showed that the presence of surfactant and water did not significantly affect this parameter. Although the expected behavior was an enhancement in the corrosion process due to the water present, this was not observed because in emulsion systems water is dispersed as small droplets inside the oil-continuous phase and surfactants can serve as corrosion inhibitors.

Table No 3 properties of Evaluated blend fuel

		Type of fuel		
Sr. no	**Properties**	**Biodiesel with 5% water**	**Biodiesel with 10 % water**	**Biodiesel with 15% water**
1	Density at 150C, (Kg/m3)	865	872	880
2	Calorific value (kJ/kg)	37455	36405	34945
3	Kinematic viscosity, cst	5	5.6	6.3
4	Flash point, 0C	180	185	190
5	Pour Point 0C	10	11	12
6	Cetane number	60	57	52
8	Copper corrosion	Class 1 max	Class 1max	Class 1 max

CONCLUSION

In present study, the preparation & characterization of water in biodiesel emulsion systems was investigated. The main conclusions can be summarized as follows:

1) Surfactant concentration has very positive effect on emulsion stability. Stabilization time of water in biodiesel emulsion increases with an increase in the consumption of surfactant. Blend of SPAN 80/TWEEN 80 at 3% concentration forms most stable Water in biodiesel emulsion
2) The blend of surfactant with HLB of 9 is the most desirable for Water in biodiesel emulsion. In other words, surfactant having HLB of 9 is most significant to make fuel emulsion.
3) Increase in water content in water in biodiesel emulsion decreases the emulsion stability. 5 % water in biodiesel emulsion has better stability

4) Density and viscosity of all studied systems were higher than those obtained for neat Biodiesel and these properties increased with increasing water content. The results for the Pour point and corrosiveness showed that the presence of surfactant and water did not significantly affect these parameters. But calorific vale and Cetane number will be decreased as the water content increases.

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