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Preparation and investigation of bio-diesel using hydrated ethanol as an alternative fuel: A comparative study

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Abstract
Free fatty acid in the available crude jatropha oil was found to be 8.1 percent. Therefore, a two-step trans-esterification process was carried out to prepare bio-diesel using hydrated ethanol as reactant. In the first step, pretreatment was carried out to reduce free fatty acid in crude jatropha oil and in second step, base catalyzed transesterification of pretreated oil was carried out to produce biodiesel. Pretreatment reaction was carried out by using (1.5%, 2%, 2.5% and 3.0% v/v of oil) H_2SO_4 and (24% and 30% v/v of oil) 150° proof, 160° proof, 170° proof, 180° proof and 190° proof ethanol for 1.5 h reaction time at temperature of 70°C respectively. Oil with minimum free fatty acid content obtained from the first step in case of each hydrated ethanol was selected for the second step and the reaction was carried out using hydrated ethanol of same proof which was used in the first step. In second process, alkali catalyzed transesterification of pretreated oil was carried using (1.5 percent, 2.0 percent, 2.5 percent and 3 percent w/v of oil) KOH and different proportions of hydrated ethanol (30%, 40% and 50% v/v of oil) for reaction time 2 h at 70°C. The maximum recovery (66.5%) was obtained when 40% of ethanol (160° proof) and 2.5% KOH was used for transesterification. Fuel properties such as kinematic viscosity, flash point, cloud point, pour point, density and gross heating value of crude jatropha oil, biodiesel and its blends were measured and then compare with diesel.

Keywords: biodiesel; ethanol; jatropha oil; diesel; transesterification

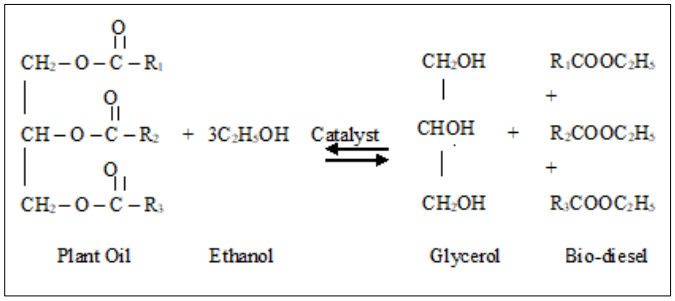
1. Introduction
Tractor and small diesel engines are the main power source for agricultural operations which has increased dependency of farmers on diesel. Due to gradual depletion of fossil fuel reserves and from the point of view of long-term energy security, it becomes necessary to operate the existing diesel engines using alternative fuels without modifying the existing engine [1-2]. There is therefore a global search for alternative fuels which could be cheaper, safer and environmentally friendly. Plant oils are renewable and can be an alternative which can be tried as a replacement for diesel fuel [3].

Edible oils such as soybean, rapeseed, canola, sunflower, cottonseed, etc. and non-edible oils like jatropha, karanja, neem, mahua etc. have been tried to supplement diesel fuel in various countries [2-8]. In U.S., biodiesel programme is based on their surplus edible oils like soybean and in Europe from rapeseed and sunflower oils. Since, India is not self-sufficient in edible oil production, hence, some non-edible oil bearing plant trees available in the country which can be exploited for biodiesel production [9].

Viscosity of plant oils are reported to be about 10 times more than that of diesel fuel, leads to poor fuel atomization and inefficient mixing with air, which contribute to incomplete combustion [10, 11] High viscosity of plant oils poses the great difficulty in using these oils in diesel engines.

There are different ways to reduce viscosity of oil such as Trans esterification, emulsification and the use of viscosity reducers [12-15]. Among these methods, Trans esterification is most commercial used method for biodiesel preparation. Tran's esterification can be carried out by using homogeneous acid/base catalyst, hetrogenous catalyst or by using lipases as biocatalyst [16]. Among these methods, base catalyzed trans esterification is the most common method.

Biodiesel is prepared by the trans-esterification process, which is a chemical process of reacting plant oil with an alcohol in the presence of a catalyst to produce glycerol and ester (Bio-diesel). Stoichiometric ally, one mole of oil reacts with three moles of alcohol to produce three moles of the biodiesel and one mole of glycerol [1, 11, 17].



Alcohol which is used as reactant in trans-esterification process can be methanol, ethanol, propanol and butanol. The lot of work has been done to produce bio-diesel using methanol as reactant. But, ethanol is produced by the fermentation of biomass, it is renewable. It contains water after distillation process. Water is removed from ethanol through distillation process up to 95% (190^0 proof). Removal of water above 95% molecular sieve is required, which is very costly and an energy extensive process.

The present study was therefore carried out to develop the process for the production of biodiesel using hydrated ethanol as reactant. The reaction conditions were optimized for maximum recovery of bio-diesel.

2. Material and Methods

2.1 Materials

The chemicals used in the experiments were hydrated ethanol, sulphuric acid, potassium hydroxide, benzene and Phenolphthalein. All reagents used were of analytical grade. Jatropha oil was selected for preparation of biodiesel.

2.2 Determination of free fatty acid content

Free fatty acid (FFA) in oil is very important factor that affects the yield of biodiesel. The free fatty acid content of crude jatropha oil was determined by titrimetric method. A known amount (1.0 g) of oil sample was taken in 250 ml flask, 20 ml of ethanol and 20 ml of benzene was added to it. Two drops of Phenolphthalein were added as indicator. Then it was titrated with aqueous solution of N/40 NaOH and the pink colour appears which persists for 30 seconds. A blank determination without addition of oil was also run with above experiment. Free fatty acid value of the sample was computed using the following expression:

$$FFA\% = \frac{N \times (B-S) \times M}{10\,W}$$

Where,

B = Volume of NaOH solution used for blank

S = Volume of NaOH used for oil

W = Weight of the oil (g)

N = Normality of NaOH solution

M = Molecular weight of fatty acids (oleic acid 282)

2.3 Methodology for preparation of bio-diesel

Free fatty acid in the crude jatropha oil was found to be 8.1 percent. Therefore, a two-step trans-esterification process was carried out to prepare bio-diesel. In the first step, free fatty acids in the oil were converted into their esters by a pretreatment process and in second step, base catalyzed Trans esterification of pretreated oil was carried out.

2.3.1 Pretreatment of crude jatropha oil

The pretreatment was carried out to reduce free fatty acid in crude jatropha oil. The crude jatropha oil was pre-heated at 70°C. Solution of hydrated ethanol and sulphuric acid as catalyst was mixed in the oil. The reaction was carried out in a round bottomed flask on a rotamantle shown in Fig. 1 at 70°C for 1.5 h. After the reaction was complete, treated oil was transferred in a separating funnel and kept undisturbed for about 5 hours. The top layer of oil was collected in beaker and placed in the oven for about 2 hours to remove excess alcohol and water vapors. The free fatty acid of pretreated oil was determined by titrimetric method. The different proportion of sulphuric acid as catalyst (1.5%, 2%, 2.5% and 3.0% v/v of oil) and hydrated ethanol (24% and 30% v/v of oil) were used to study their effect on reduction in free fatty acid content of oil.

Fig 1: Rotamantle

2.3.2 Base catalyzed trans-esterification of pre-treated oil

The acid pretreated oil was used in second step to produce biodiesel using base catalyzed Trans esterification. Oil with minimum free fatty acid content obtained from the first step in case of each hydrated ethanol was selected for the second step and the reaction was carried out using hydrated ethanol of same proof which was used in the first step. Acid pretreated Jatropha oil was placed in a round bottom flask and heated up to 70°C. The catalyst (weight amount) was dissolved in ethanol and the resulting mixture was poured into flask containing pre-treated oil. Then, the reaction mixture was stirred continuously by maintaining steady temperature of 70 °C for 2 hours. After the reaction, mixture was poured from the flask into separating funnel shown in figure and kept undisturbed for 48 hours for phase separation by gravity settling. Bio-diesel from top layer was decanted and washed with distilled water. The bio-diesel was washed until excess of KOH and alcohol was removed. After washing, it was heated in an oven to remove water. The study was conducted using different proportion of catalyst (1.5 percent, 2.0 percent, 2.5 percent and 3 percent w/v of oil) and different proportions of hydrated ethanol (30%, 40% and 50% v/v of oil) to identify the suitable conditions of base-catalyzed trans-esterification reaction to get maximum biodiesel yield.

2.4 Preparation of blends

Five different blends of diesel and bio-diesel were prepared for determination of fuel properties. The blends prepared are mentioned below:

1. B5 = 5% bio-diesel + 95% diesel
2. B10 = 10% bio-diesel + 90% diesel

3. B15 = 15% bio-diesel + 85% diesel
4. B20 = 20% bio-diesel + 80% diesel
5. B25 = 25% bio-diesel + 75% diesel

2.5 Fuel Properties

Property	Unit	Measuring Device
Kinematic viscosity	centistoke	VISGAGE
Flash point	°C	Pensky-Martens closed cup
Cloud point and pour point	°C	Cloud and pour pint apparatus
Gross heating value	°C	Bomb calorimeter

3. Results and Discussion

3.1 Preparation of bio-diesel using hydrated ethanol as reactant

Free fatty acid content in the available Jatropha crude oil was 8.10%. Due to high free fatty acid content, two-step trans-esterification process was adopted to prepare bio-diesel using hydrated ethanol as reactant.

The first step was mainly a pretreatment for the reduction of free fatty acid content in the oil. Pretreatment reaction was carried out using different hydrated ethanol as reactant like 150˚ proof, 160˚ proof, 170˚ proof, 180˚ proof and 190˚ proof ethanol. Different combinations of hydrated ethanol and acid catalyst were tried.

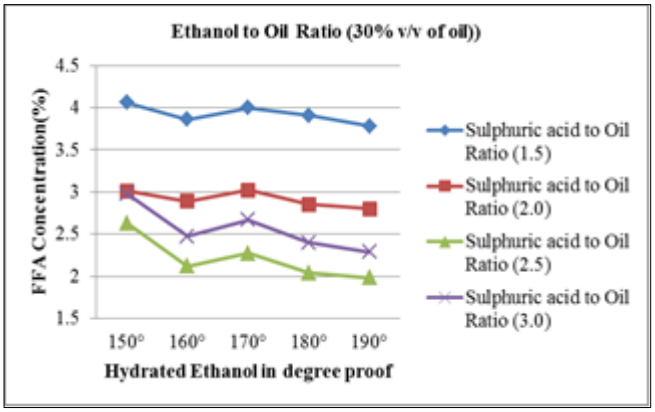


Fig 2: FFA concentration vs Hydrated ethanol in degree proof for 24% v/v of oil

Fig. 3 FFA concentration vs Hydrated ethanol in degree proof for 30% v/v of oil

It was observed that with the increase in quantity of H_2SO_4 from 1.5% to 2.5% (v/v of oil) in the reaction the free fatty acid content of oil decreased but further increase of H_2SO_4 from 2.5% to 3.0% (v/v of oil) resulted in increase of free fatty acid in the oil. With the increased of ethanol from 24% to 30% (v/v of oil) the free fatty acid content in oil decreased in case of all the hydrated ethanol. When 1.5% H_2SO_4 and 24% ethanol was used in the reaction the reduction in free fatty acid content of oil was minimum for all the hydrated ethanol but 2.5% H_2SO_4 and 30% hydrated ethanol resulted in maximum reduction of free fatty acid content in oil.

The minimum free fatty acid content of 2.63, 2.12, 2.27, 2.04 and 1.98% were obtained in case of 150° proof, 160° proof, 170° proof, 180° proof and 190° proof ethanol respectively (Table 4.1). Oil with minimum free fatty acid content obtained from the first step in case of each hydrated ethanol were selected for the second step and the reactions were carried out using hydrated ethanol of same proof which was used in the first step for each oil.

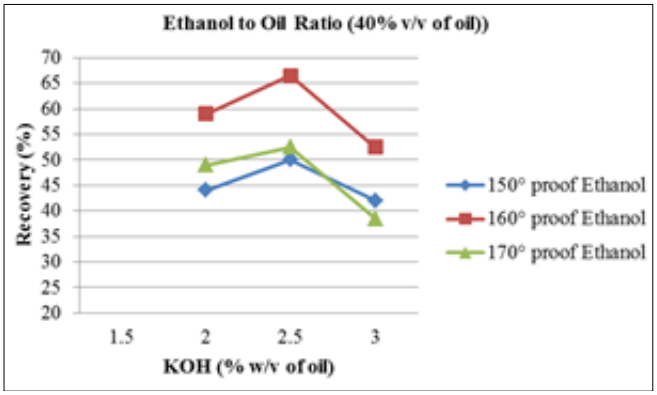


Fig 3: Recovery vs KOH for 30% v/v of Ethanol to oil

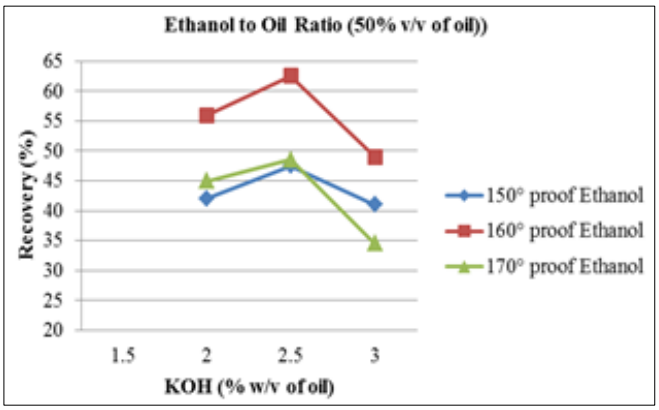


Fig 4: Recovery vs KOH for 50% v/v of Ethanol to oil

In the second step in case of 180° proof and 190° proof ethanol the recovery of biodiesel were nearly nil for all combinations of KOH (1.5, 2.0, 2.5 and 3.0 5w/v of oil) and ethanol (30, 40 and 50%v/v of oil). The recovery of biodiesel using different proportions of 150° proof, 160° proof, 170° proof ethanol are shown in fig. The maximum recovery (66.5%) was obtained when 40% of 160° proof ethanol and 2.5% KOH was used for the reaction.

Based on the results obtained, the process parameters selected for pretreatment of oil in first step for bulk production of biodiesel were:

Table 1: Parameters selected for bulk production of bio-diesel

Proof of ethanol	160˚
Ratio of ethanol	30% (v/v of oil)
Ratio of catalyst (H_2SO_4)	2.5% (v/v of oil)
Reaction temperature	70˚C
Reaction time	1.5 h

The process parameters selected for trans-esterification in second step for bulk production of biodiesel were:

Proof of ethanol	160˚
Ratio of ethanol	40% (v/v of oil)
Ratio of catalyst (KOH)	2.5% (w/v of oil)
Reaction temperature	70˚C
Reaction time	2.0 h

3.2 Fuel properties of Jatropha oil, diesel, bio-diesel of Jatropha oil and their blends with diesel

3.2.1 Kinematic viscosity

The kinematic viscosity of diesel (B0), Jatropha oil and bio-diesel (B100) were found to be 4.16, 39.66 and 8.83 cSt respectively. The results indicated that the Jatropha oil had the

kinematic viscosity 9.5 times higher than that of diesel. Kinematic viscosity of pure bio-diesel (8.83 cSt) was found to be more than double than that of diesel (4.16 cSt), but the blends B5 and B10 had the viscosity closer to that of diesel. The kinematic viscosity of the blends increased with the increase of content of bio-diesel in the blends shown in figure.

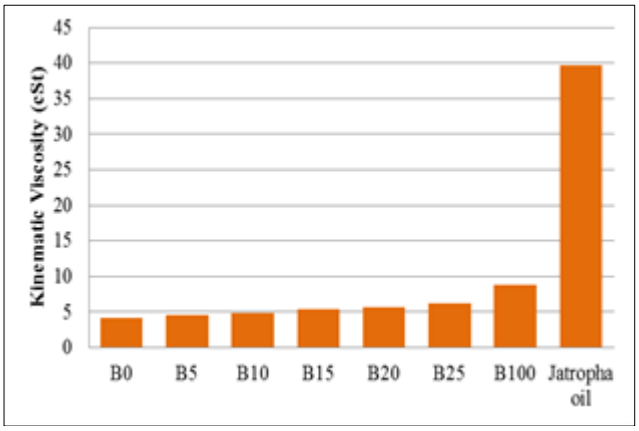


Fig 5: Kinematic viscosity of different fuels

3.2.2 Gross heating value

The gross heating value of diesel, jatropha crude oil and bio-diesel were found to be 44.61, 34.23 and 38.23 MJ/kg respectively. The heating value of the blend decreased with increase of bio-diesel in the blend but decrease in heating value was very small as shown in figure.

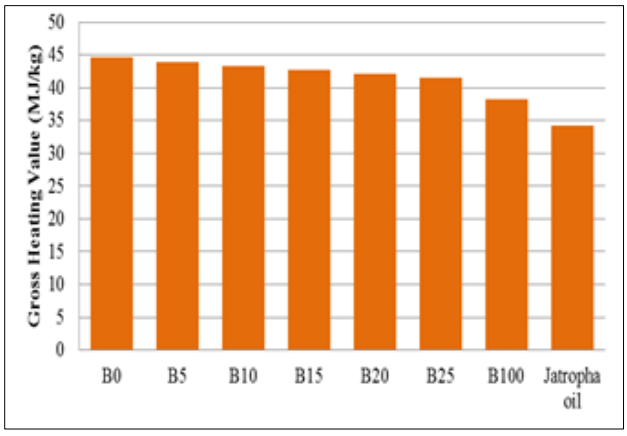


Fig 6: Gross heating value of different fuels

3.2.3 Flash point

The flash point of diesel used in the experiment was 59.66°C and in case of jatropha oil it was more than four times than that of diesel. The flash point of different blends decreased with increase of bio-diesel in the blend. Since, the bio-diesel had higher flash point temperature, the increase of bio-diesel in the blend increased the flash point of blend having more percentage of bio-diesel as shown in figure.

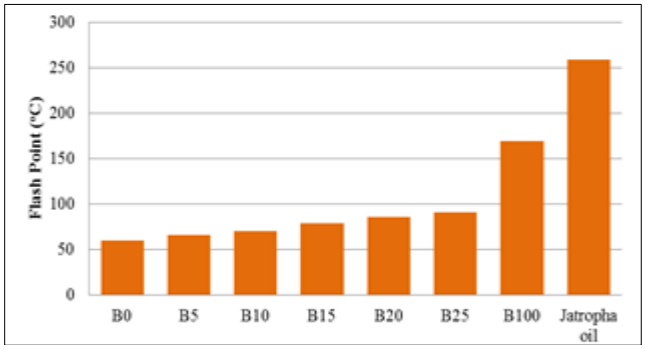


Fig 7: Flash point of different fuels

3.2.4 Density

Density of diesel used in the experiments was found to be 0.838 g/cm^3 whereas the density of Jatropha oil and bio-diesel were 0.944 and 0.892 g/cm^3. Since bio-diesel was found to be heavier than diesel, the density of blends increased with increase of bio-diesel in the blend shown in figure.

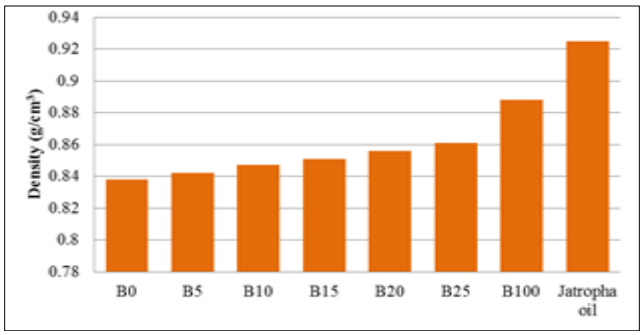


Fig 8: Density of different fuels

3.2.5 Cloud point

Cloud point was found 6.7, 0.8 and 2.8°C for jatropha crude oil, diesel and biodiesel respectively. Cloud point of blends increased with increase of bio-diesel in the blend shown in figure.

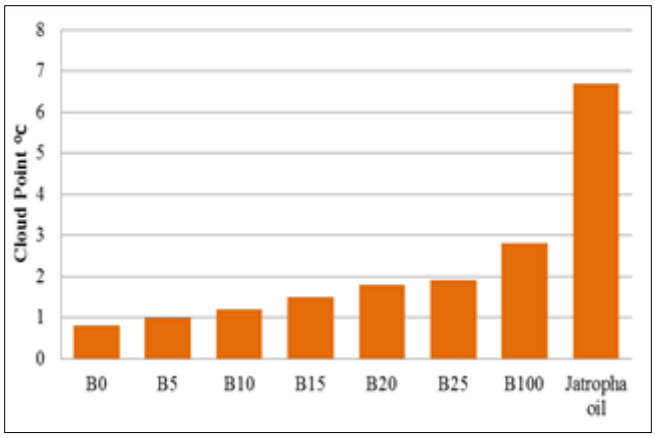


Fig 9: Cloud point of different fuels

3.2.6 Pour point

Pour point of diesel, jatropha crude oil and bio-diesel were found to be -6.1, 2.6 and -2.3°C respectively. Pour point of B5, B10, B15, B20, B25 and B100 were found to be higher than that of diesel.

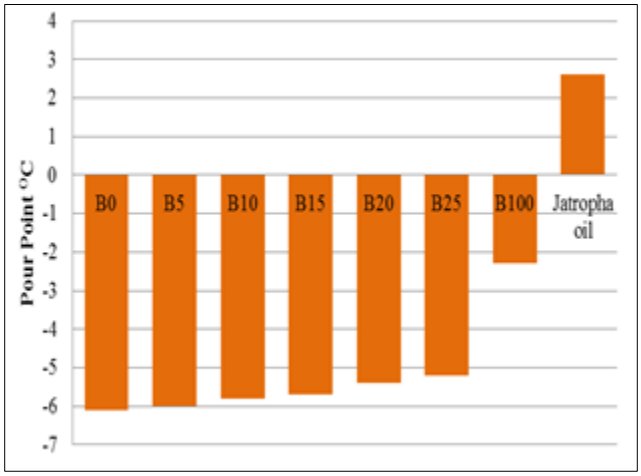


Fig 10: Pour point of different fuels

4. Conclusions

In the present study, bio-diesel was prepared using hydrated ethanol as reactant having different moisture contents and different process parameters. Most suitable hydrated ethanol and process parameters for better recovery of bio-diesel were selected for the bulk production of bio-diesel.

Blends of diesel and biodiesel were prepared by mixing 5, 10, 15, 20 and 25% biodiesel in diesel and designated as B5, B10, B15, B20 and B25 respectively. The following conclusions are made based on experimental results.

1. Free fatty acid content in the available Jatropha crude oil was 8.10%. Due to high free fatty acid content, two-step trans-esterification process was adopted to prepare bio-diesel using hydrated ethanol as reactant.
2. The minimum free fatty acid content of 2.63, 2.12, 2.27, 2.04 and 1.98% were obtained by using 2.5% (v/v of oil) H_2SO_4 and 30% (v/v of oil) 150° proof, 160° proof, 170° proof, 180° proof and 190° proof ethanol respectively.
3. The maximum recovery (66.5%) was obtained when 40% of ethanol (160° proof) and 2.5% KOH was used for trans-esterification.

The fuel characteristics of prepared biodiesel and their blends were compared with diesel fuel to find its potential use in compression ignition engine.

5. Acknowledgements

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