

# Synthesis of Jatropha Oil based Biodiesel using Environmentally Friendly Catalyst and their Blending Studies with Diesel

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**Abstract** Jatropha oil is readily available as one of the cheapest non-food feedstock in India. In this work, we would like to explore the use of Zirconium based heterogeneous catalysts to synthesis Jatropha oil biodiesel (JBD) and to take advantages of the solid nature as well as reusability of the environmentally friendly heterogeneous catalyst. In order to compare JBD was also synthesized using conventional sodium methoxide (NaOMe homogenous catalyst). Best yield was obtained using heterogeneous catalyst (ZrH<sub>3</sub>). Synthesized JBD by both homogenous and heterogeneous catalysts were characterized by FTIR, and Diesel Fuel Properties like viscosity and density. Viscosities of synthesized all JBD were in agreement with ASTM D-6751 (100%-BD) and ASTM D-975 (100%-Diesel). In this study, Blending studies of Jatropha biodiesel-JBD (5 %) with diesel was also carried out and diesel fuel properties like viscosity, density, pour point and flash point were also investigated. Except density of blended mixture, all other fuel properties studied are in agreement with ASTM D-975 (100%-Diesel). 5% JBD Blend have nearly same physical properties as that of petro-diesel which demonstrates that it would be commercially viable to use in the field. This study will help biodiesel producer to be competitive in production of Jatropha based biodiesel, using heterogeneous catalyst and work up process would be eased and reuse catalyst. Thus it provides the economic pathway for the synthesis of eco-friendly biodiesel.

**Keywords** Bio-diesel, Jatropha Oil, Non-Edible Feedstock, Heterogeneous, Homogenous Catalysts

## 1. Introduction

Due to increase usage of fossil fuels, we are in a position to go through scarcity. Goal of this study is to reduce the utilization of fossil fuels and obtain diesel from non-edible feed stocks without destructing supply from edible oil. This requirement has opened up the new door for energy sources from the bio-based materials like plant oil. More-over, due to famous food v/s fuel debate, scientists are considering non-food as bio-energy source to prepare bio-fuel like biodiesel. Biodiesel is Fatty Acid Methyl Ester obtained from plant oil after reacting it with Methanol in presence of homogenous catalyst like sodium methoxide<sup>1</sup>. However, homogenous catalyst has following limitation, which makes them environmentally non-friendly. a) Soluble in the reaction mixture which forms emulsion and to break, it requires long time b) Catalyst is not separated after reaction and c) Pure product with less yield. Heterogeneous

catalyst offers following advantages and make them more environmentally friendly a) Insoluble in the reaction mixture which offers easier work up process b) Catalyst can be separated easily-so one can reuse catalyst and c) More yield with less tedious purification process.

Recently, we have reported preparation of biodiesel using transesterification of non edible feedstock like [Jatropha oil<sup>2</sup>, and Wild Brazilian mustard (*Brassica juncea* L.)<sup>3</sup>] with methanol using sodium methoxide as homogenous catalyst. In further study, we reported Jatropha methyl acetate as other class of biodiesel, which was produced using direct acetylation of the jatropha alcohol<sup>4</sup>. We have also reported composition and physical properties studies of non-edible oils of field pennycress (*Thlaspi arvense* L.) and (*Lepidium sativum* L.)<sup>5</sup>, arugula, shepherd's spurge, and upland cress oils<sup>6</sup>. Jatropha oil is readily available as one of the cheapest non-food feedstock in India. With this in view, to explore the use of heterogeneous catalyst as Eco-friendly for synthesis of the Jatropha oil based bio-diesel (JBD), current work was undertaken. In this work blending studies of JBD (5%) with commercially available diesel was also proposed in order to demonstrate its viability for transport vehicle (real world application).

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## 2. Experimental

### 2.1. Materials

Jatropa Oil (CSMCRI = 870 g/mole), Dichloromethane (GR-MERCK) as a solvent, Methanol (GR-MERCK), Sodium Hydroxide pellets (MERCK). Petro-diesel was purchased from the petro outlet in Baroda, Gujarat, India. All the materials were used directly without any prior purification.

The solid acid catalysts for Biodiesel synthesis, 12-Tungstophosphoric acid supported on hydrous Zirconia (ZH<sub>3</sub>) and 12-Tungstosilic acid supported on hydrous Zirconia (ZS<sub>3</sub>) were prepared by the method reported in literature<sup>7-8</sup>. Catalyst-1 as 12-Tungstosilic acid hydrous Zirconia (ZS<sub>3</sub>) and Catalyst-2 as 12-Tungstophosphoric acid hydrous Zirconia (ZH<sub>3</sub>).

### 2.2. Procedure

#### 2.2.1. Preparation of Jatropa oil bio-diesel (JBD) using Heterogeneous catalysts (ZS<sub>3</sub>)

The transesterification of Jatropa oil with methanol was carried out in a three necked round bottom flask of cap. 250 ml equipped with water condenser, mechanical stirrer, and a thermometer pocket. Jatropa oil sample (1 mole), methanol (6 mole), and 1.0 g of ZS<sub>3</sub> with dichloromethane as a solvent was taken. The temperature of the reaction is increased to 60°C with continuous stirring at 1200 rpm for 4 h in oil bath. After, reaction was completed, reaction mixture was transferred into separating funnel. Glycerol was allowed to settle down by gravity. Glycerol layer was removed and dichloromethane solvent added in reaction mixture and was shaken. Organic layer was washed with distilled water till neutral pH=7 was achieved. With continuous stirring the organic layer was then poured over Sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>) in flask and allowed to stand for 15 minutes. Then it was filtered. The excess of dichloromethane was then evaporated using rotatory evaporator.

The weight of the product was 7.6 g (using the ZS<sub>3</sub> Catalyst) % Yield = 92 %

#### 2.2.2. Preparation of Jatropa oil bio-diesel (JBD) using Heterogeneous catalysts (ZH<sub>3</sub>)

The transesterification of Jatropa oil with methanol was carried out in a three necked round bottom flask of cap. 250 ml equipped with water condenser, mechanical stirrer, and a thermometer pocket. Jatropa oil sample (1 mole), methanol (6 mole), and 1.0 g of ZH<sub>3</sub> with dichloromethane as a solvent was taken. The temperature of the reaction was increased to 60°C with continuous stirring at 1200 rpm for 4 h in oil bath.

After, reaction was completed, reaction mixture was transferred into separating funnel. Glycerol was allowed to settle down by gravity. Glycerol layer was removed and dichloromethane solvent added in reaction mixture and was shaken. Organic layer was washed with distilled water till neutral pH=7 was achieved. With continuous stirring the

organic layer was then poured over Sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>) in flask and allowed to stand for 15 minutes. Then it was filtered. The excess of dichloromethane was then evaporated using rotatory evaporator.

The weight of the product was 7.8 g (using the ZH<sub>3</sub> Catalyst) % Yield = 95 %.

#### 2.2.3. Preparation of Jatropa oil bio-diesel (JBD-SM) using Homogeneous catalysts (30 % Sodium Methoxide solution in Methanol)

250 ml single necked round bottom flask equipped with the water condenser was taken on oil bath. 150 g of Jatropa oil, 25 gm of methanol, and 10 g of Sodium methoxide solution in methanol was taken in above flask. The whole reaction mixture was allowed to stir for 4 hrs at 600 rpm on magnetic stirrer. The reaction temperature was maintained at 65°C. The reaction mixture was turned to creamish white in color. The whole mixture was washed with the brine solution to break the resultant emulsion formed during the reaction.

The reaction mixture was further transferred to the separating funnel for separation of two phases. The upper phase consisted of methyl ester with small amount of impurities such as residual alcohol, glycerol and partial glycerides, while the lower portion consisted of glycerol. The upper methyl ester layer collected was further purified by distilling residual methanol at 60°C.

The weight of the product was 134.60 g (using the CH<sub>3</sub>ONa Catalyst) % Yield = 89.7 %

The product was further used for the functional group characterization using the Fourier Infrared Spectroscopy-FTIR (Figure 1 and 2) as well as Diesel Fuel Properties like kinematic viscosity, density, pour point and flash point as shown in Table 1.

#### 2.2.4. Blending studies of Bio-diesel with Petro-diesel

In Blending studies of bio-diesel with petro-diesel, 5.0 ml of the Jatropa based biodiesel (JBD) + 95.0 ml of petro-diesel was mixed and stirred vigorously for 30 minutes and tested for different fuel properties like viscosity, density, pour point as well as flash point and data were reported in Table 2.

### 2.5. Characterization

#### 2.5.1. Fourier Infrared Spectroscopy- FTIR

FT-IR spectra of the compounds were recorded on Shimadzu-8400S spectrophotometer by KBr pellet method. The spectra were obtained over the frequency range 4000-400 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>. The FT-IR spectra of samples are shown in Figure 1-2.

#### 2.5.2. Diesel, Biodiesel and Blend Fuel Properties Studies by ASTM Method

Viscosity in cSt, and Density (g/ml) of Diesel, Jatropa Oil (JO), Jatropa based bio-diesel (JBD) and its blend with Diesel fuel properties were characterized using ASTM

D-6751 (Standard for 100% BD)<sup>1</sup> and ASTM D-975 (Standard for 100% Diesel)<sup>10</sup>.

### 3. Results and Discussion

Jatropha biodiesel (JBD) was synthesized using transesterification of Jatropha oil with methanol in presence of either homogenous catalyst (Sodium Methoxide, JBD-SM) or heterogeneous catalysts (ZS<sub>3</sub>, JBD-ZS<sub>3</sub> and ZH<sub>3</sub>, JBD-ZH<sub>3</sub>).

Characterization of the JBD for functional group determination was carried out using the using FTIR as shown in Figure 1-2.

The IR spectrum (Figure 1) for Jatropha Oil (JO) shows the ester linkage of triglyceride at 1745 cm<sup>-1</sup>. The IR spectrum (Figure 2) of Jatropha Bio-diesel (JBD-ZH<sub>3</sub>) shows the ester linkage of Fatty Acid Methyl Ester at 1741 cm<sup>-1</sup>.

When we compare the FTIR of the Figure 2 with the baseline - JO (Figure 1), it clearly shows that Carbonyl group of the JO is shifted from 1745 to 1741 cm<sup>-1</sup>, which

indicates that number of carbonyl group is decreased. JBD is Fatty Acid Methyl Ester containing only one carbonyl group compare to baseline JO, which originally contains three carbonyl groups

This observation is in consistent with recently reported FTIR spectra of the JBD report by EPA<sup>9</sup>, which also supports that synthesized product is the bio diesel. There is no alcohol or un-reacted methanol which have broad absorption in the range of 3600-3500 cm<sup>-1</sup>.

Same discussion is true for the other catalyst ZS<sub>3</sub>.

#### 3.1. 100% Jatropha Based Bio-diesel

Table-1 describes different parameters likes percentage yield of JBD, Carbonyl group frequency in cm<sup>-1</sup> in FTIR, Viscosity in cSt, and Density (g/ml) of Jatropha Oil (JO) and JBD. It also shows comparison of Viscosity in cSt, and Density (g/ml) of Jatropha Oil (JO) as well as JBD with ASTM D-6751 (Standard for 100% BD)<sup>1</sup> and ASTM D-975 (Standard for 100% Diesel)<sup>10</sup>.

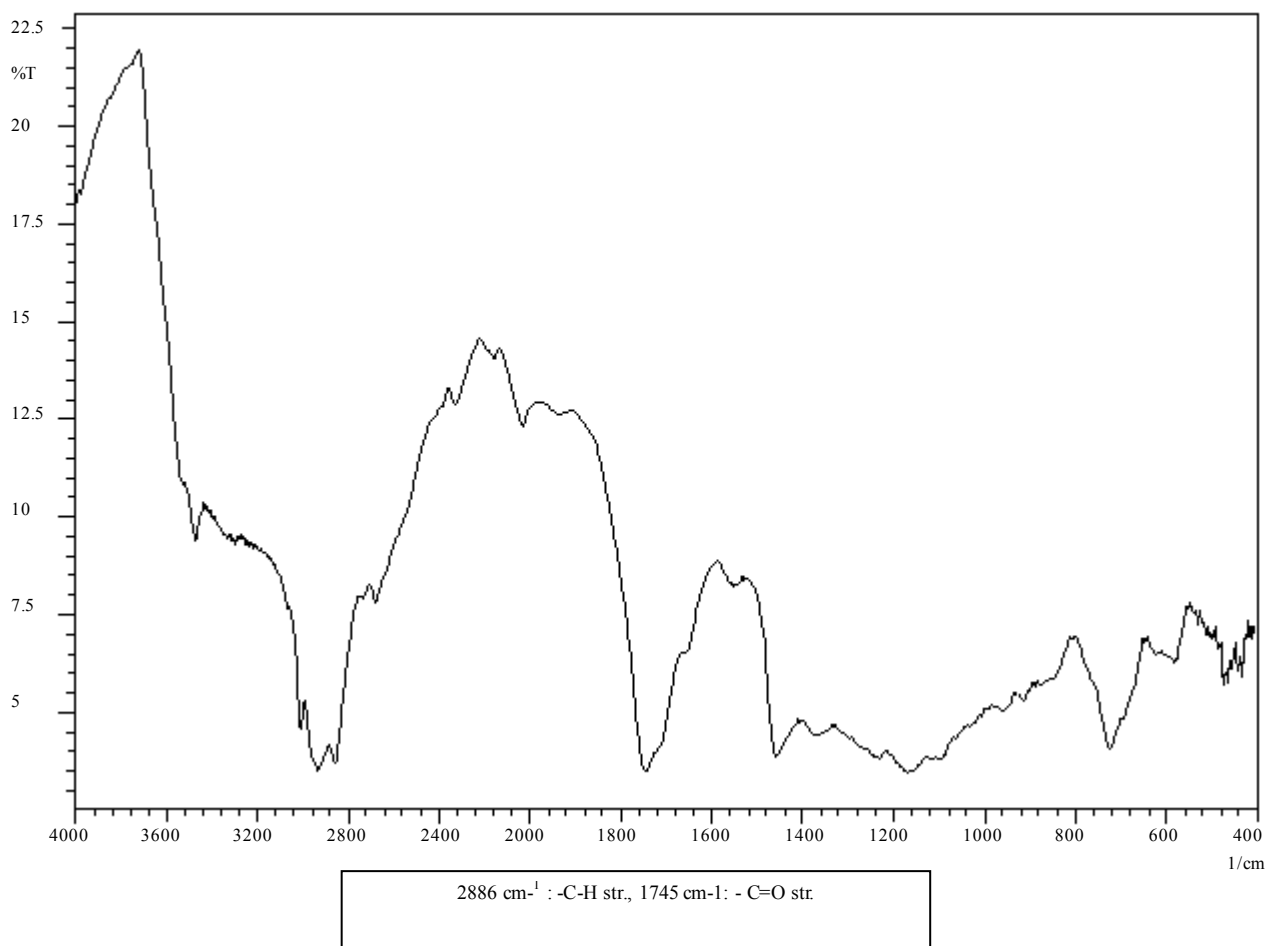
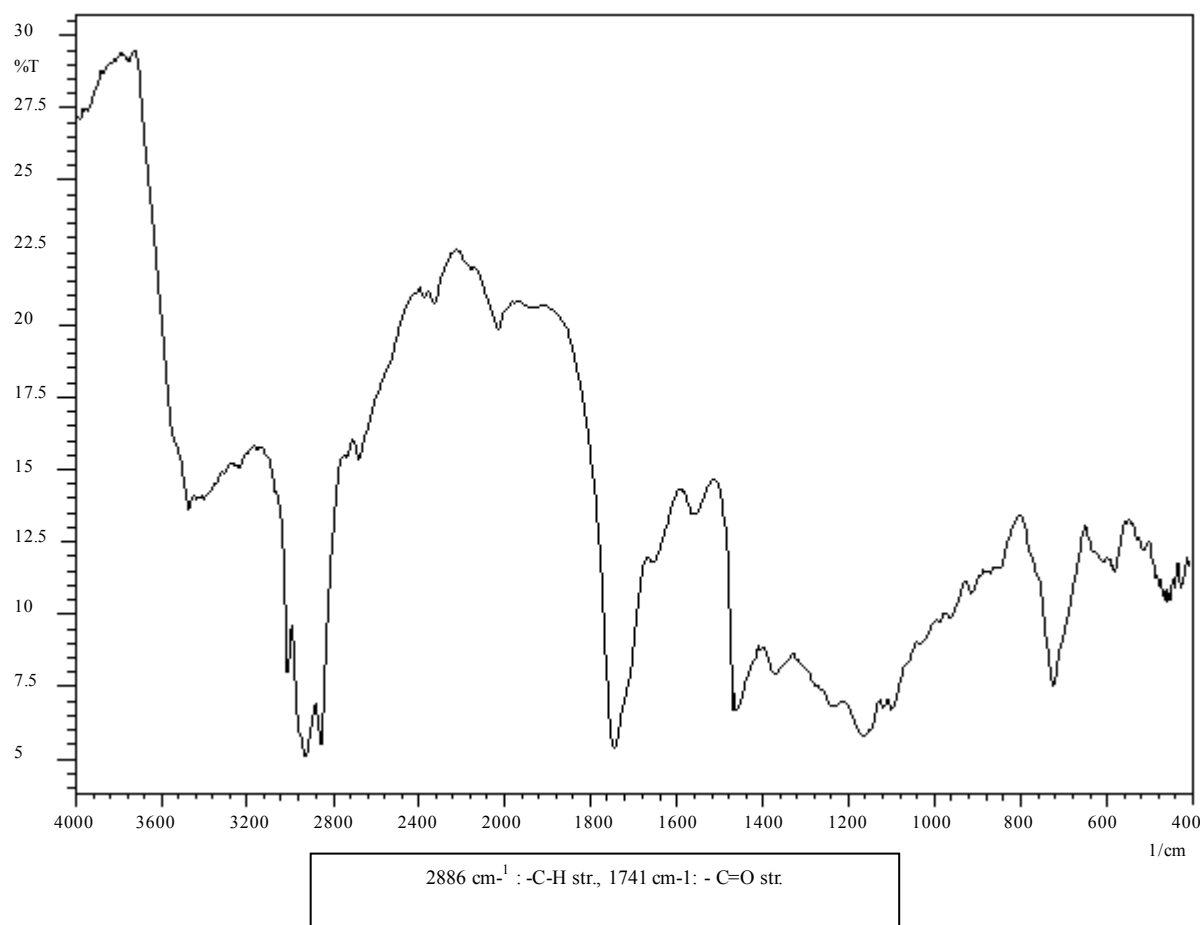


Figure 1. IR Spectra of Jatropha Oil

**Figure 2.** IR Spectra of Biodiesel using  $\text{ZH}_3$ **Table 1.** JO and JBD-100%

Parameters/Oil or BD	Jatropha oil	BD- $\text{ZH}_3$	BD- $\text{ZS}_3$	BD-SM	ASTM D-6751 for 100% BD	ASTM D-975 for Diesel
Yield in %	-	95	92	90	-	-
FT-IR for -C=O $\text{cm}^{-1}$	1745	1741	1741	1741	-	-
Viscosity (cSt)	53	4.6	4.4	3.8	1.9-6.0	1.3-4.1
Density (g/ml)	0.92	0.88	0.85	0.88	0.88	0.85

**Table 2.** Blending studies of Jatropha biodiesel (5%) with diesel

Test Name	BD- $\text{ZH}_3$	BD- $\text{ZS}_3$	BD-NaOMe	Diesel For current studies	ASTM D975 for Diesel
Viscosity (cSt)	4.2	4.3	4.1	4.1	1.3-4.1
Density (g/ml)	0.82	0.81	0.81	0.81	0.85
Flash Point ( $^{\circ}\text{C}$ )	66	67	63	65	60-80
Pour point ( $^{\circ}\text{C}$ )	-16	-14	-18	-17	-35 to -15

From Table 1 it is clear that in heterogeneous catalysts  $\text{ZH}_3$  gives best yield (95%) compare to  $\text{ZS}_3$  (92%). Even in comparison to classical homogeneous catalyst, sodium methoxide (90% yield),  $\text{ZH}_3$  gives best yield.

Table 1, it is also displayed that Jatropha oil has viscosity 53 cSt and density 0.92 g/ml.

Viscosities of synthesized all JBD were in agreement with ASTM D-6751 (100%-BD) and ASTM D-975 (100%-Diesel)

which also clearly indicates that JO (53 cSt) has been converted into JBD (4.6 – 3.8 cSt) Densities of synthesized JBD- $\text{ZH}_3$  and JBD-SM were in agreement with ASTM D-6751 (100%-BD) while JBD-  $\text{ZS}_3$  was in agreement with ASTM D-975 (100%-Diesel).

### 3.2. Blending studies of Jatropha biodiesel-JBD (5 %) with diesel

Table-2 describes Blending studies of Jatropha biodiesel-JBD (5 %) with diesel and their different fuel properties like Viscosity in cSt, and Density (g/ml), Flash point (°C) and Pour Point (°C). It also shows comparison of Blending studies of Jatropha biodiesel-JBD (5 %) with diesel with ASTM D-6751 ASTM D-975<sup>10</sup> (Standard for 100% Diesel).

Except density of above mentioned blended mixture, all other properties studied are in agreement with ASTM D-975 (100%-Diesel). Thus 5% JBD Blend have nearly same physical properties as that of petro-diesel used for current studies which demonstrates that it would be commercially viable for use in the field.

## 4. Conclusions

Current study has demonstrated the use of the heterogeneous catalyst based on Zirconium for the synthesis of the Jatropha oil biodiesel. 5% JBD Blend have nearly same physical properties as that of petro-diesel which demonstrates that it would be commercially viable for use in the field. This study will help biodiesel producer to be competitive in the production of Jatropha based biodiesel, using heterogeneous catalyst which has easier work up process as well as reusability of the catalyst. Thus it provides the economic pathway for synthesis of eco-friendly biodiesel.

Further studies will continue using more heterogeneous catalysts and by blending higher percentage of JBD with petro-diesel and study their fuel properties .

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