

Review Article

# Heterogeneous Catalysts for Biodiesel Synthesis from Karanja Oil by Transesterification Process

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## Abstract

The heterogeneous catalysts are playing an important role and are perspective catalysts in future for biodiesel production. These heterogeneous catalysis features lower corrosiveness, environmental friendliness, easy catalyst recovery and high process integrity, all at levels superior to those of homogeneous catalysis. The heterogeneous basic catalyst includes oxides of Magnesium, Aluminum and Calcium etc. All sort of experiments were conducted by using the engine. The performance and emission results obtained were analyzed and discussed. The different blends of Karanja Biodiesel were compared with fossil fuel diesel. From observations it could be concluded that the blends of Karanja with diesel up to 20% by volume could replace diesel for running the diesel engine with less emissions without modifying the engine and without sacrificing the power output. This will thus help in controlling air pollution to a great extent.

**Keywords:** Biodiesel synthesis, Transesterification, Heterogeneous, catalyst.

## 1. Introduction

Diesel fuels are used in many areas and have importance for the economy of countries. Because of the energy and global warming crisis, development of renewable energies, for example, H<sub>2</sub> energy, solar energy and biodiesel have been focused worldwide. Biodiesel is made entirely from vegetable sources; it does not contain any sulphur, aromatic hydrocarbons, metals or crude oil residues. Due to the properties like high degradability, no toxicity, low emission of carbon monoxide, particulate matter and unburned hydrocarbons, Biodiesel has gained international attention as a source of alternative fuel. Biodiesel can be used in conventional compression ignition engines, which need almost no modification. Experimentation is done with Karanja oil methyl ester and their blends. The performance and emission results obtained were analyzed and discussed.

### Karanja

It is available in Western Ghats of India. The average life of Karanja tree is 80-100 years. It grows naturally; having very deep roots to reach water, and is one of the few crops well-suited to commercialization by India's large population of rural poor. The tree is hardy, reasonably drought resistant and tolerant to salinity.

The Karanja tree is of medium size, reaching a height of 15-25 meters. The tree bears green pods which after some 10 months change to a tan color. The pods are flat to elliptic, 5-7 cm long and contain 1 or 2 kidney shaped brownish red kernels. The yield of kernels per tree is reported between 8 to 24 kg. The oil content varies from 27% to 39%. Comparison between Homogeneous and Heterogeneous Catalyst.

	Homogeneous Catalyst	Heterogeneous Catalyst
<b>Phase</b>	Liquid	Liquid, Gas, Solid
<b>Diffusivity</b>	High diffusivity. Having all reactants and catalyst in one phase enhances dramatically the diffusivity under proper stirring.	Diffusivity might be an issue for catalysts with low surface area.
<b>Catalyst Separation</b>	The separation of the products from the catalyst is generally expensive, the only exception being in biphasic catalysis.	The separation of the products from the catalyst is usually straightforward.
<b>Recycling</b>	Recycling is expensive due to difficult treatment of the spent catalyst.	Recycling is usually straightforward, although the catalyst might need reactivating treatment.
<b>Heat Transfer</b>	High Heat Transfer. Having all reactants and catalyst in one phase enhances dramatically the heat transfer under proper stirring.	Heat Transfer might be an issue due to the different heat capacities of reactants and catalyst.

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### Advantages of Heterogeneous catalyst

- 1) Excess methanol is removed by vaporization and recycled to the process with fresh methanol.
- 2) The catalyst is very stable with no metal leaching.
- 3) There is no formation of either glycerate salts or metal soaps.
- 4) No neutralization step is required,
- 5) No introduction of water. (No washing)
- 6) No salt formation.
- 7) These accounts for exceptional purity glycerol that is free of water and salt.
- 8) There is no waste production of low-value fatty acids.
- 9) This Process is economical.

### 2. Research work

The three different biodiesels were produced with the following three different feed stocks and heterogeneous catalyst separately. The properties of biodiesel and its blends have been checked and compared with diesel fuel are given below. The engine performance tests have been carried out for different compression ratios. The performance and emission results have been studied as follows.

#### Karanja oil and SiO<sub>2</sub> catalyst



Fig.1 Transesterification setup

### 3. Experimental setup and specifications

Set up under test is Kirloskar TV1 VCR having 3.5 HP @ 1500 Rpm, One Cylinder, Four Stroke, Constant Speed, Water Cooled, Diesel Engine



Fig.2 Engine set up

### Engine Specifications

Make	Kirloskar
No. of Cylinders	1
No. of Strokes	4
Type of Cooling	Water Cooled
Power Developing Capacity	3.5 kW @ 1500 rpm
Compression Ratio Range	12-18
Stroke	110 mm
Bore	87.5 mm
Cylinder Volume	661

#### 3.1 Preparation of blends of biodiesel

At present the amount of biodiesel available is less than that of diesel. The biodiesel blended with diesel by volume as B10 (10% Karanja biodiesel & 90% diesel fuel), B20 (20% Karanja biodiesel & 80% diesel fuel), B30 (30% Karanja biodiesel & 70% diesel fuel), B40 (40% Karanja biodiesel & 60% diesel fuel), B50 (50% Karanja biodiesel & 50% diesel fuel), B100 (100% Karanja biodiesel & 00% diesel fuel). Then the samples were proceed for testing of properties.

#### 3.2 Karanja oil and SiO<sub>2</sub> catalyst

Biodiesel is produced from Karanja oil using heterogeneous SiO<sub>2</sub> catalyst. Tested Physical Properties of the Diesel, Karanja Biodiesel and its Blends are as follows

Sr.No	Test Description	Ref. Std. ASTM	Reference		Diesel	Karanja Biodiesel Blends					Karanja Oil
			Unit	Limit		B00%	B10%	B20%	B40%	B60%	
1	Density	D1448	gm/cc	0.80-0.90	0.835	0.838	0.843	0.85	0.858	0.874	
2	Calorific Value	D6751	MI/Kg	34-45	42.5	42.3	42.12	41.27	40.35	38.8	
3	Cetane No.	D613	-	41-55	49.5	49.4	49.62	50.35	50.6	51.5	
4	Viscosity	D445	mm <sup>2</sup> /sec	03-1um	2.7	-	-	-	-	5.32	
5	Moisture	D2709	%	0.05%	NA	NA	NA	NA	NA	0.04	
6	Flash Point	D93	°C	-	64	-	-	-	-	144	
7	Fire Point	D93	°C	-	71	-	-	-	-	157	
8	Cloud Point	D2500	°C	-	-6	-	-	-	-	7	

### 3.3 Performance Characteristics

Experiments were conducted by using the engine. The performance and emission results obtained were analyzed and compared with fossil fuel diesel. The study of Karanja oil Biodiesel is discussed here in detail.

### 4. Result Table Performance Characteristics

Blend	CR	Load	BP	BTHE	mech eff	sfc
B10	16	3	0.89	11.08	11.49	0.77
	16	6	1.73	16.66	30.19	0.51
	16	9	2.6	19.7	31.71	0.44
	17	3	0.89	12.16	12.47	0.7
	17	6	1.76	16.73	22.26	0.51
	17	9	2.65	20.17	31.14	0.43
	18	3	0.89	10.32	14.97	0.83
	18	6	1.72	15.33	25.37	0.56
	18	9	2.59	18.91	35.67	0.45
B20	16	3	0.92	11.47	12.43	0.75
	16	6	1.73	16.87	19.37	0.51
	16	9	2.6	20.69	28.76	0.41
	17	3	0.89	11.34	9.63	0.76
	17	6	1.75	17.15	22.4	0.5
	17	9	2.6	20.63	28.11	0.42
	18	3	0.89	11.52	9.67	0.74
	18	6	1.79	17.96	15.43	0.48
	18	9	2.6	21.18	22.87	0.4
B40	16	3	0.95	11.56	8.82	0.74
	16	6	1.78	19.47	13.13	0.44
	16	9	2.61	19.54	20.6	0.44
	17	3	0.94	11.68	8	0.73
	17	6	1.78	17.38	13.28	0.49
	17	9	2.61	19.59	19.42	0.44
	18	3	0.89	11.36	6.94	0.75
	18	6	1.79	17.58	14.76	0.49
	18	9	2.6	20.7	22.66	0.41
B60	16	3	0.95	11.38	8.86	0.75
	16	6	1.78	16.59	18.42	0.52
	16	9	2.6	19.18	21.28	0.45
	17	3	0.89	10.61	8.87	0.81
	17	6	1.78	17.06	17.06	0.5
	17	9	2.63	19.91	23.23	0.43
	18	3	0.94	11.36	8.99	0.75
	18	6	1.72	16.46	15.3	0.52
	18	9	2.62	20.39	22.78	0.42
D	16	3	0.93	9.92	16.61	0.86
	16	6	1.75	18.01	27.34	0.57
	16	9	2.62	18.67	36.78	0.46
	17	3	0.93	10.92	14.9	0.79
	17	6	1.8	16.82	24.33	0.51
	17	9	2.61	20.27	32.33	0.42
	18	3	0.93	11.24	14.88	0.76
	18	6	1.79	17.1	24.24	0.5
	18	9	2.58	20.43	33.66	0.42

### 4.1 Result Table of Emission Characteristics

Blends	CR	Load	CO	HC	CO2
D	16	3	0.02	8	0.6
	16	6	0.03	11	0.6
	16	9	0.03	14	0.4
	17	3	0.02	10	0.8
	17	6	0.01	11	0.6
	17	9	0.01	12	0.6
	18	3	0.03	13	1
	18	6	0.02	14	0.9
	18	9	0.02	13	0.6
B10	16	3	0.02	16	0.7
	16	6	0.02	17	0.6
	16	9	0.01	17	0.5
	17	3	0.02	9	0.7
	17	6	0.01	14	0.8
	17	9	0.01	15	0.5
	18	3	0.02	10	0.8
	18	6	0.01	12	0.7
	18	9	0.01	15	0.6
B20	16	3	0.02	18	0.7
	16	6	0.02	18	0.7
	16	9	0.01	18	0.7
	17	3	0.02	5	0.8
	17	6	0.01	9	0.7
	17	9	0.01	7	0.4
	18	3	0.02	8	0.8
	18	6	0.01	11	0.7
	18	9	0.01	10	0.6
B40	16	3	0.01	11	0.8
	16	6	0.01	13	0.7
	16	9	0.01	14	0.5
	17	3	0.02	11	0.8
	17	6	0.01	12	0.8
	17	9	0.01	13	0.6
	18	3	0.02	12	0.9
	18	6	0.01	7	0.7
	18	9	0.01	9	0.6
B60	16	3	0.02	14	0.8
	16	6	0.01	10	0.7
	16	9	0.01	12	0.5
	17	3	0.02	7	0.8
	17	6	0.01	10	0.7
	17	9	0.01	9	0.6
	18	3	0.02	10	0.8
	18	6	0.01	9	0.7
	18	9	0.01	9	0.5

A) Performance Characteristics

Brake Power

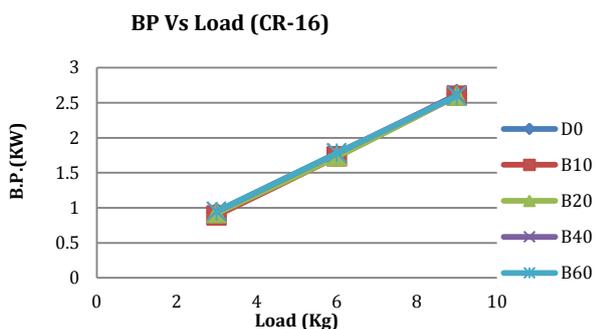


Fig.3 Variation of BP with load for Karanja biodiesel

The variation of brake thermal efficiency with brake power for diesel, Karanja biodiesel and their blends are shown in Fig 3 for CR-16, it is observed that brake power increase with load in all cases. Brake power is more or less equal with diesel at all loads for B10, B20, B40, B60 blends.

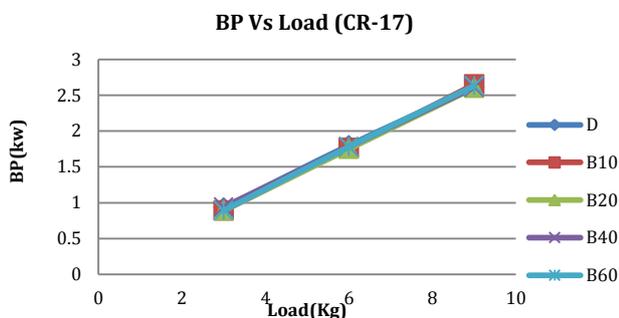


Fig.4 Variation of BP with load for Karanja biodiesel

The variation of brake thermal efficiency with brake power for diesel, Karanja biodiesel and their blends are shown in Fig. 4 for CR-17, it is observed that brake power increase with load in all cases. Brake power is more or less equal with diesel at all loads for B10, B20, B40, B60 blends.

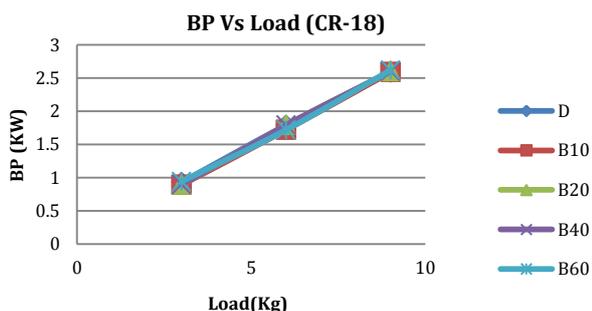


Fig.5 Variation of BP with load for Karanja biodiesel

The variation of brake thermal efficiency with brake power for diesel, Karanja biodiesel and their blends are

shown in Fig. 5 for CR-18, it is observed that brake power increase with load in all cases. Brake power is more or less equal with diesel at all loads for B10, B20, B40, B60 blends.

Specific Fuel Consumption (sfc)

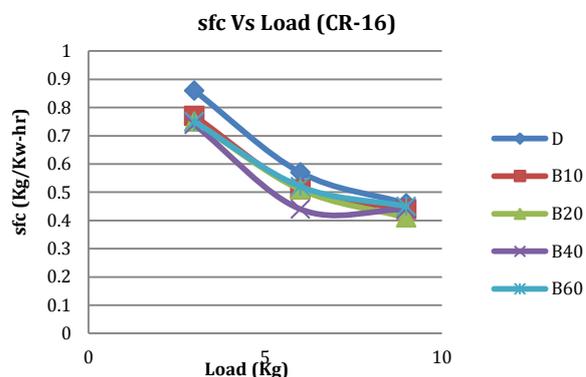


Fig. 6 Variation of BSFC with load for Karanja biodiesel

The variation of BSFC with load for Karanja biodiesel at CR 16 is given in fig.6. It is found that BSFC of diesel fuel is higher than other biodiesel blends at load 3 kg and 6 kg while it is near to same at 9kg load. The BSFC for blends B10% and B20% shows its performance near to diesel fuel.

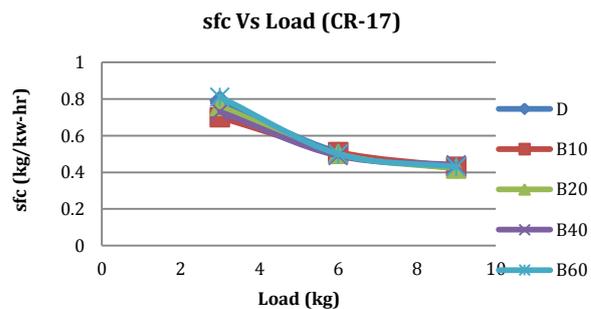


Fig. 7 Variation of BSFC with load for Karanja biodiesel

The variation of BSFC with load for Karanja biodiesel at CR 17 is given in fig.7. It is found that BSFC of diesel fuel is higher than other biodiesel blends at load 3 kg while it is near to same at 6kg, 9kg load.

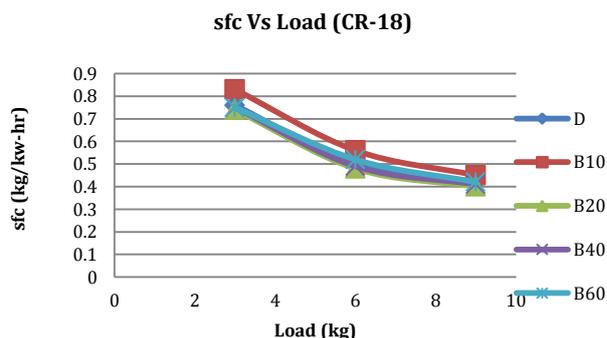
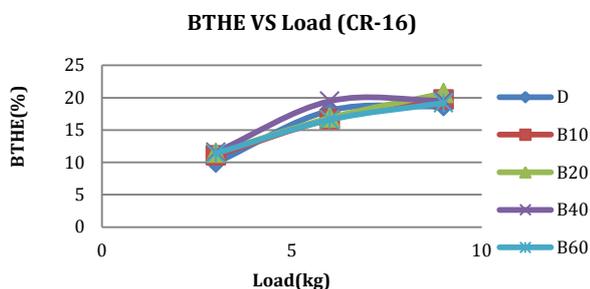


Fig.8 Variation of BSFC with load for Karanja biodiesel

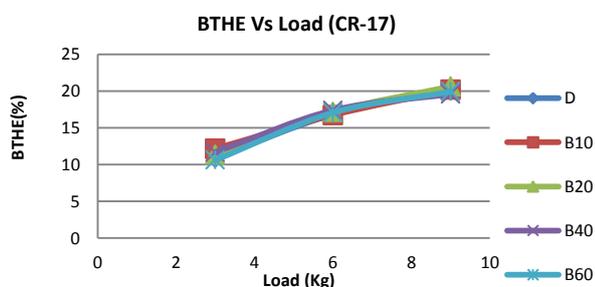
The variation of BSFC with load for Karanja biodiesel at CR 17 is given in fig.8. It is found that BSFC of diesel fuel is nearly equal to other biodiesel blends at all loads. The bsfc of B10 is higher than diesel at all loads.

*Brake Thermal Efficiency*



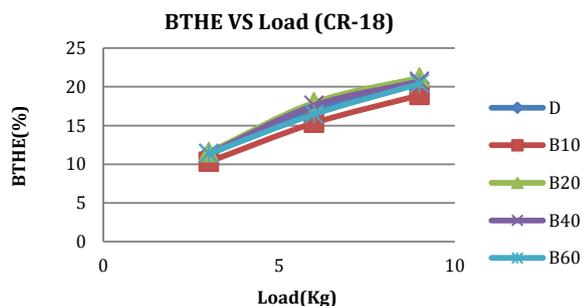
**Fig.9** Variation of BTHE with load for Karanja biodiesel

The variation of brake thermal efficiency with load, for diesel and Karanja biodiesel blends is shown in fig.9. The Brake Thermal Efficiency for B20 and B40 at lower load is more or less equal to that of diesel. At higher load the Brake Thermal Efficiency increases for B20 and B40 blends.



**Fig.10** Variation of BTHE with load for Karanja biodiesel

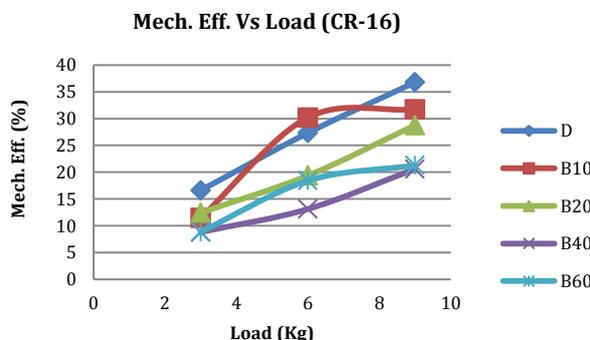
The variation of brake thermal efficiency with load, for diesel and Karanja biodiesel blends is shown in fig.10. The Brake Thermal Efficiency for B20 and B40 at lower load is more or less equal to that of diesel. At higher load the Brake Thermal Efficiency increases for B20 and B40 blends.



**Fig.11** Variation of BTHE with load for Karanja biodiesel

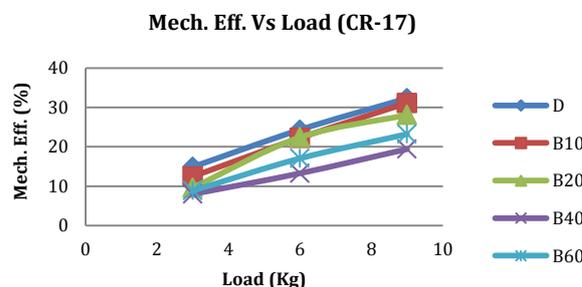
The variation of brake thermal efficiency with load, for diesel and Karanja biodiesel blends is shown in fig.11. The Brake Thermal Efficiency for B20 and B40 at lower load is more or less equal to that of diesel. At higher load the Brake Thermal Efficiency increases for B20 and B40 blends

*Mechanical Efficiency*



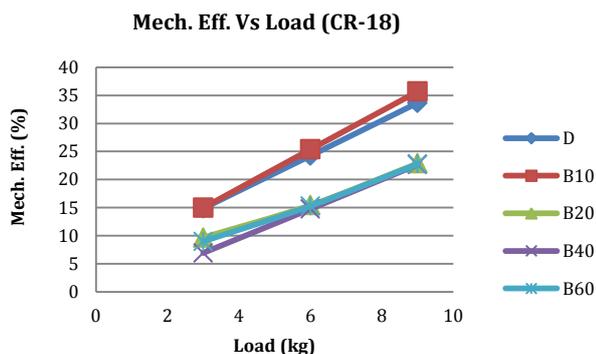
**Fig.12** Variation of Mech. Eff. with load for Karanja biodiesel

The variation of mechanical efficiency with brake power, for diesel and Karanja blends is shown in fig.12. The mechanical efficiency of diesel is slightly higher than the Karanja biodiesel. Mechanical efficiency of 10% blend is very close to diesel, followed by 20% blend for entire range of operation. Maximum mechanical efficiency of 10% and 20% blend is 31.71% and 28.76% against, 36.78% of diesel oil. From the graph it is evident that with increase in concentration of Karanja biodiesel in neat diesel oil decreases the mechanical efficiency. This may be due to better lubricating property of the diesel which reduces frictional losses.



**Fig.13** Variation of Mech. Eff. with load for Karanja biodiesel

The variation of mechanical efficiency with brake power, for diesel and Karanja blends is shown in fig.13. The mechanical efficiency of diesel is slightly higher than the Karanja biodiesel. Mechanical efficiency of 10% blend is very close to diesel, followed by 20% blend for entire range of operation. Maximum mechanical efficiency of 10% and 20% blend is 31.71% and 28.76% against, 36.78% of diesel oil.

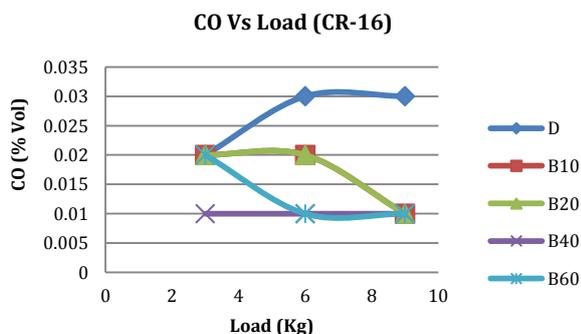


**Fig.14** Variation of Mech. Eff. with load for Karanja biodiesel

The variation of mechanical efficiency with brake power, for diesel and Karanja blends is shown in fig.14. The mechanical efficiency of diesel is slightly higher than the Karanja biodiesel. Mechanical efficiency of 10% blend is very close to diesel for entire range of operation. Maximum mechanical efficiency of 10% blend is 35.67% and 33.66% of diesel oil.

*B) Emission Characteristics*

*Carbon monoxide*

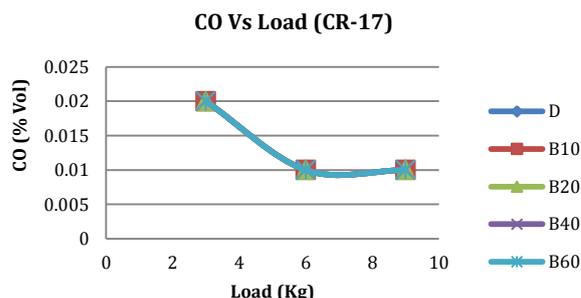


**Fig. 15** Variation of CO with load for Karanja biodiesel

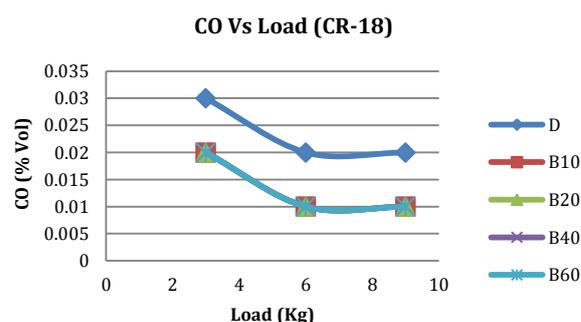
Fig.15 shows the variation of carbon monoxide emission with load for Karanja biodiesel and its blends in the test engine. The CO emission depends upon the strength of the mixture, availability of oxygen and viscosity of fuel. CO emission of all blends is lower than that of diesel. Among the blends 40% blend has a lower CO emission followed by 60% blend. CO emission of 10% and 20% blends is same and lower at maximum load about 0.01%. CO emission of pure diesel is higher than all other blends for entire operating range and maximum of 0.03% occurs at the rated load. This is due to incomplete combustion at higher loads which results in higher CO emissions.

Fig.16 shows the variation of carbon monoxide emission with load for Karanja biodiesel oil and its blends in the test engine for CR-17. The emission of CO is decreases with increase of loads for pure diesel and all biodiesel blends. The value of CO emission is

minimum at full load about 0.01% by Vol. and maximum at lower load about 0.02% by Vol.



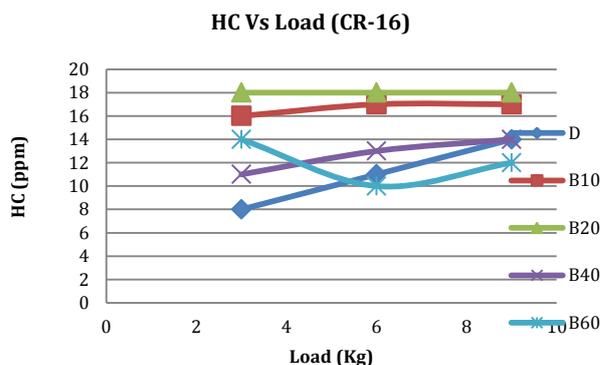
**Fig. 16** Variation of CO with load for Karanja biodiesel



**Fig.17** Variation of CO with load for Karanja biodiesel

Fig.17 shows the variation of carbon monoxide emission with load for Karanja biodiesel oil and its blends in the test engine at CR-18. CO emission of all blends of biodiesel and pure diesel decreases with increase of load. CO emission of pure diesel is higher than all other blends for entire operating range and maximum of 0.03% of vol. occurs at minimum load and minimum of 0.02% of vol. at maximum load. CO emissions of all blends are maximum of 0.02% of vol. at lower load value and minimum of 0.01% vol. at the rated load.

*Unburned Hydro Carbon*



**Fig.18** Variation of HC with load for Karanja biodiesel

Fig 18 shows the variation of emission of hydrocarbon with load for different blends of Karanja biodiesel and

pure diesel. The emission of HC is increasing with increase of loads. UHC of pure diesel has lower emission compared with all other biodiesel blends followed by 40% blend. The value of UHC of pure diesel and blend 40% is maximum about 14 ppm and 16 ppm respectively. The minimum value of UHC for both pure diesel and 40% is 8 ppm and 11 ppm respectively.

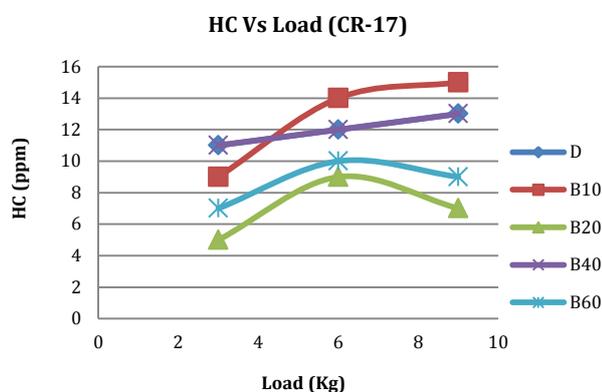


Fig.19 Variation of HC with load for Karanja biodiesel

Fig 19 shows the variation of emission of hydrocarbon with load for different blends of Karanja biodiesel and pure diesel. The emission of HC is increasing with increase of loads. UHC of pure diesel and 10% biodiesel blend have approximately similar performance characteristic. The 20% blend has lower emissions compared with all other biodiesel blends followed by 60% blend. 20% blend has lower UHC emission about, 5 ppm at minimum load and 7 ppm at maximum load.

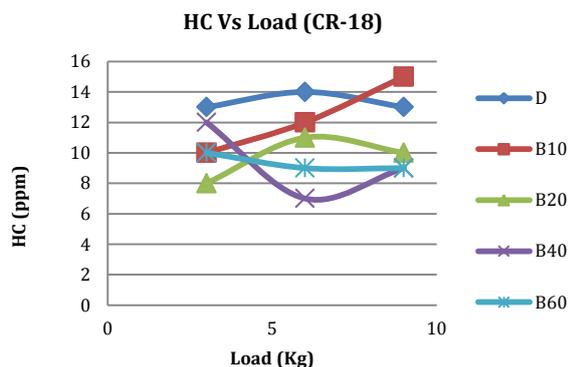


Fig.20 Variation of HC with load for Karanja biodiesel

Fig 20 shows the variation of emission of hydrocarbon with load for different blends of Karanja biodiesel and pure diesel at CR-18. The emission of HC is increasing with increase of loads. UHC of pure diesel has lower emission compared with all other biodiesel blends followed by 10% blend. The value of UHC of pure diesel and blend 10% is maximum about 13ppm and 15ppm at higher respectively loading condition. The minimum value of UHC for both pure diesel and 10% is 13 ppm and 10 ppm respectively at lower loading condition. As blending of biodiesel increases in pure diesel UHC emission decreases.

Carbon Dioxide (CO<sub>2</sub>)

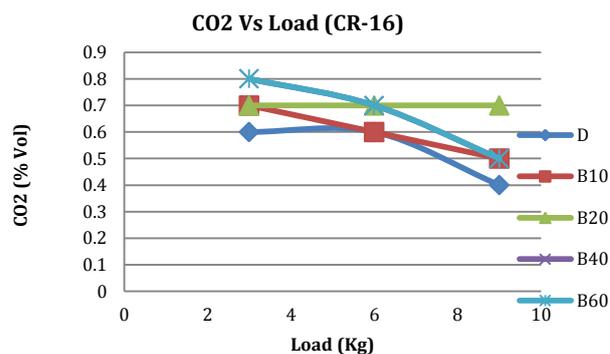


Fig.21 Variation of CO<sub>2</sub> with load for Karanja biodiesel

Fig.21 shows the variation of carbon dioxide emission with load for Karanja biodiesel oil and its blends in the test engine. CO<sub>2</sub> emissions for pure diesel and all biodiesel blends decreases with increase in load. Among all the blends 10% blend has a lower CO<sub>2</sub> emission followed by 20% blend. CO<sub>2</sub> emission of 60% blend is higher than all other blends for entire operating range and maximum at minimum load and minimum occurs at the rated load about 0.5%. CO<sub>2</sub> emission of pure diesel is lower than all other blends for entire operating range and minimum of 0.4 % occurs at the rated load.

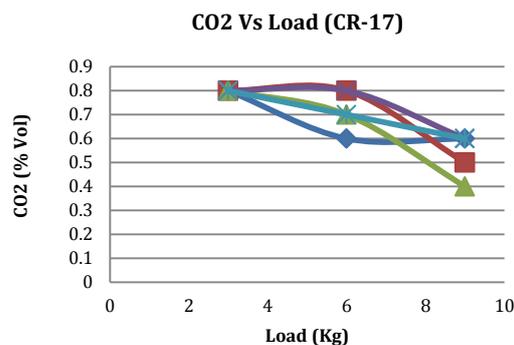
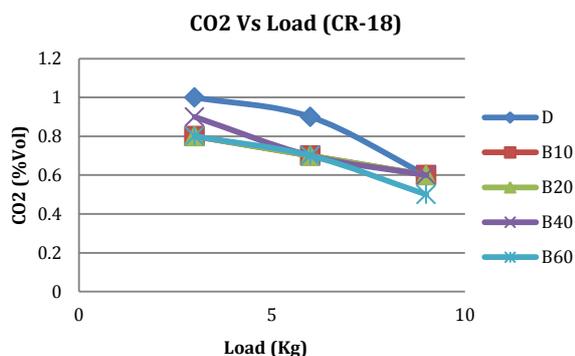


Fig.22 Variation of CO<sub>2</sub> with load for Karanja biodiesel

Fig.22 shows the variation of carbon dioxide emission with load for Karanja biodiesel oil and its blends in the test engine for CR-17. CO<sub>2</sub> emissions for pure diesel and all biodiesel blends decreases with increase in load. Among all the blends 10% blend has a lower CO<sub>2</sub> emission followed by 20% blend. CO<sub>2</sub> emission of 40% blend is higher than all other blends for entire operating range and maximum at minimum load and minimum occurs at the rated load about 0.6%. CO<sub>2</sub> emission of pure diesel is lower than all other blends for entire operating range and minimum of 0.6 % occurs at the rated load.

Fig.23 shows the variation of carbon dioxide emission with load for Karanja biodiesel oil and its blends in the test engine at CR-18. CO<sub>2</sub> emissions for pure diesel and all biodiesel blends decreases with increase in load.



**Fig.23** Variation of CO<sub>2</sub> with load for Karanja biodiesel

Pure diesel has higher CO<sub>2</sub> emissions than biodiesel blends of maximum 1% vol. at lower load and minimum of 0.6% vol. at higher load. Among all the blends 60% blend has a lower CO<sub>2</sub> emission followed by 20%, 30%, 40% blends of maximum 0.9% vol. at lower load and minimum of 0.6% vol. at higher load. At higher loading condition CO<sub>2</sub> emissions of blends and pure diesel are same and minimum.

## Conclusion

There is a growing interest in the development of heterogeneous catalyst. The emphasis laid on the application of heterogeneous catalyst is mainly to overcome the limitation incurred by homogeneous one. Increasing biodiesel consumption requires optimized production processes that are compatible with high production capacities and that feature simplified operations, high yields, and the absence of special chemical requirements and waste streams. In the heterogeneous process, the catalyst is very stable with no metal leaching. There is no formation of either glycerate salts or metal soaps which affords the following advantages: no neutralization step is required, there is no introduction of water and there is no salt formation; these accounts for exceptional glycerol purity. In addition, there is no waste production of low-value fatty Acids. A heterogeneous catalyzed continuous process gives these objectives to be attained. A simple method was found to recover the basic sites to regenerate the catalyst that performed good activity and reproducibility.

The effects of Karanja biodiesel fuel on performance, emission of VCR diesel engine have been investigated and compared with base line diesel fuel.

The main observations are as follows:

- 1) Brake power is nearly equal to diesel fuel at all loads for all blends of biodiesel.
- 2) BSFC is nearly equal to diesel fuel at higher load.
- 3) Brake thermal efficiency at higher compression for biodiesel and its blends decreases due to lower heating value of biodiesel and its injection of higher quantities compared to diesel for the same load conditions.

- 4) Mechanical efficiency decreases for biodiesel and its blends as compared to diesel, as percentage of biodiesel increase in pure diesel.
- 5) The emission of CO decreases as percentage of biodiesel increases; this is due to oxygen present in biodiesel which converts CO in CO<sub>2</sub>.
- 6) At full load condition HC emissions obtained is higher for B10 while for other blends HC emissions are equal to or less than diesel this is due to complete combustion of fuel at higher compression ratio.
- 7) At lower compression ratio emission of CO<sub>2</sub> is higher for biodiesel blends this is due to oxygen present in biodiesel which convert CO into CO<sub>2</sub>.
- 8) From all these observations it could be concluded that the blends of Karanja with diesel up to 20% by volume could replace diesel for running the diesel engine with less emissions without modifying the engine and without sacrificing the power output. This will thus help in controlling air pollution to a great extent.

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