

Green Chemical Preparation And Biological Evolution Of Biodiesel From Industrial Waste Oil Using Ceramic-Based Novel Catalysts

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Abstract: Continuous increase in oil prices, shortage of fossil fuel, and the big problem of carbon dioxide emission have encouraged scientists and technologists to find other new sources of energy or to develop technologies for the sustainable utilization of fuel. To resolve the above problems, renewable energies with lower environmental pollution impact need to be considered. Nowadays, several new and renewable energies have been emphasized like Nuclear Energy, Ocean Energy, Hydrothermal Energy, Biomass Energy, Geothermal Energy, etc., in which biomass energy is one of the important renewable energy sources among them. In the present scenario, most biodiesel is produced by using Edible Oils, due to which some big problems have been created viz. Food Crisis, Large expanse of the area to grow, Capital cost, Future Aspects, More Research is still required. The choice of proper catalyst as per cost-effectiveness, as well as environment friendly and high performance, is still a big problem. Investigation on analysis of biodiesel is still incomplete, and most of the available methods of analysis are hazardous. Determination of the Biological Activity of Biodiesel Samples is still a big issue for research.

Keywords: Biodiesel, Industrial Waste Oil, Ceramic-based Catalysts, Biological Activity.

I. INTRODUCTION

The necessity of energy in the entire world is consistently expanding because of the expanding populace, new innovations, new results of current life, and so forth. The main energy needed in the entire world is oil-based energy. Oil is the biggest single wellspring of energy that is being devoured by the total populace, surpassing any remaining energy assets like flammable gas, coal, atomic and inexhaustible together. The worldwide utilization of petrol and other fluid fills expanding persistently from the most

recent twenty years [1]. Along with these lines, energy accessibility later on, especially from petroleum derivatives, is an intense issue in the present situation. Another serious issue is a nonstop climb in Green House gases, particularly Carbon dioxide, emanations because of which Global Warming is expanding around the world. Albeit, to control the emanation of ozone harming substances, numerous endeavors have been done around the world, yet as indicated by current circumstances, in view of an unnatural weather change impact, the worldwide surface temperature is probably going to expand 1.1°C to 6.4°C somewhere in the range of 1990 and 2100 [2]. So the constant expansion in oil costs, lack of petroleum product, and the large issue of carbon dioxide emanation have urged researchers and technologists to discover other new wellsprings of energy or to create advancements for the feasible usage of fuel. To determine the above issues, sustainable power sources with lower natural contamination sway should be thought of. These days a few new and sustainable power sources have been underlined like Nuclear Energy, Ocean Energy, Hydrothermal Energy, Biomass Energy, Geothermal Energy, and so forth in which biomass energy is one of the significant sustainable power sources among them [3]. Biomass energy incorporates fluid biofuels got from biomass which is promising as elective energizes with low natural effect and can possibly in part supplant oil-based powers. Despite the fact that there are numerous sorts of Biofuels, however, at present, scientists are accentuating, especially on Biodiesel in light of its ecological advantages and the way that it is produced using sustainable sources and can be arranged locally [4]. Since India is insufficient in eatable oils, along these lines, Industrial Waste oil like from Food Industries could be the alluring hotspot for India for the creation of biodiesel [5]. Mechanical waste oil, like waste eatable oil, is created from the food industry isn't reused or simply used to plan bad quality and unfortunate food items. It is because of



the non-accessibility of innovation and mindfulness. The decision of legitimate impetus according to cost adequacy just as climate well disposed and superior is as yet a major issue. The present research work has been carried out on Industrial Waste oil from Bhujia Industries of Bikaner City, and a method has been developed for the preparation of biodiesel using the principles of Green chemistry. Biodiesel is defined as the monoalkyl ester of long-chain fatty acid derived from a renewable feedstock. Characteristic properties of biodiesel such as kinematic viscosity, cetane number, heating value, cloud point, density, Spectral properties, pour point, and flash point have been determined. Parameters with respect to different blends have also been determined.

II. MATERIALS AND METHODS:

Samples of Industrial Waste Oil were collected from food (Specially Bhujia Industries) industries of Bikaner. Methanol, Ethyl alcohol- (95% by volume, neutral), Phenolphthalein indicator (1gm of phenolphthalein dissolved in 100 ml of ethyl alcohol), Starch solution, Concentrated HCl, KI solution, Standard thiosulphate solution, Standard aqueous KOH solution of 0.1 Normality, Potassium dichromate, All AR Grade. The conventional Diesel Samples were collected from the Local Petrol Diesel Station. Four ceramics-based catalysts have been synthesized for the Transesterification process of various oil samples by two different methods, first is the Conventional Solid-State Ceramic Method, and another is Green Chemical Method. So a total of Eight Ceramic based Catalysts have been used in the present study.

SYNTHESIS OF CERAMIC-BASED CATALYSTS BY CONVENTIONAL SOLID-STATE CERAMIC METHOD

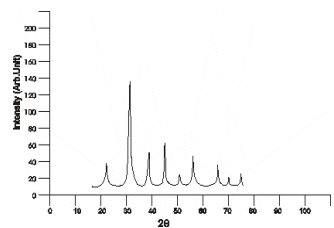
Appropriate amounts of various oxides and carbonates were accurately weighed and mixed manually in agate mortar and

pestle for six hours using acetone as a mixing medium. The mixed powders were dried, ground for half an hour, and calcined in a covered high purity alumina crucible. The calcined powders were ground and mixed uniformly with a few drops of 2 % solution of Polyvinyl alcohol (PVA), which was added as a binder. These powders were pressed into cylindrical pellets having a thickness in the range of 1-2 mm and a diameter of 12 mm using a hydraulic press. A load of 70 Kilo Newton was used to prepare pellets of all the compositions in all the systems. These pellets were kept in a platinum crucible, covered with a platinum lid and heated slowly to 773 K, and kept at this temperature for about two hours to burn off the binder completely. Thereafter, the temperature was raised to the required sintering temperature at which both sintering, as well as solid state reaction amongst various constituents, took place. These pellets were maintained at their respective firing temperatures for a sufficiently long duration. The calcination temperature, calcination time, sintering temperature, sintering time for the various systems have also been given in **Table 1**. After firing, the furnace was cooled at the rate of 5°C per minute up to 600°C, and then the power supply was switched off. The sintered pellets were ground, and powder x-ray diffraction patterns were recorded using a Philips X-ray Diffractometer (model) employing Cu-K α radiation using a Ni filter. (Fig.I). The pellets were polished, and the flat surfaces were coated with Ag paint which was cured at 100°C for 15 min. AC conductance (G), capacitance (C), and dielectric loss (D) were measured (Fig.II) using a Hioki 3532-50 LCR Hi Tester as a function of frequency (0.1 – 1000 KHz) in the temperature range 300-500K with a bias voltage of 1Volt[6-8]. All four catalysts, prepared by Solid-State Ceramic Method have been written in this paper as follows:

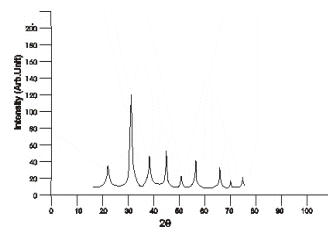
1. BaTiO₃: Catalyst A-SSR
2. Ba_{0.93}Nd_{0.07}TiO₃: Catalyst B-SSR
3. Nd_{0.70}Ba_{0.30}MnO₃: Catalyst C-SSR
4. NdMnO₃: Catalyst D-SSR

Table 1: Raw materials, Calcination Temperature, Calcination Time, Sintering Temperature, and Sintering Time for the preparation of different catalysts by Solid-State Ceramic Method.

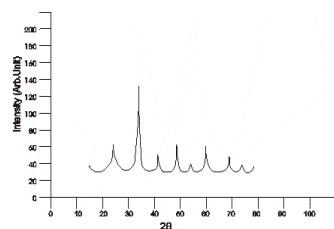
System	Raw Materials	Calcination Temp. (°C)	Calcination Time (Hrs.)	Sintering Temp. (°C)	Sintering Time (Hrs.)
BaTiO ₃ Catalyst A-SSR	BaCO ₃ , TiO ₂	1150	6	1250	12
Ba _{0.93} Nd _{0.07} TiO ₃ Catalyst B-SSR	BaCO ₃ , TiO ₂ , Nd ₂ O ₃	1100	6	1200	12
Nd _{0.70} Ba _{0.30} MnO ₃ Catalyst C-SSR	BaCO ₃ , MnCO ₃ , Nd ₂ O ₃	1100	6	1200	10
NdMnO ₃ Catalyst D-SSR	MnCO ₃ , Nd ₂ O ₃	1150	6	1250	10



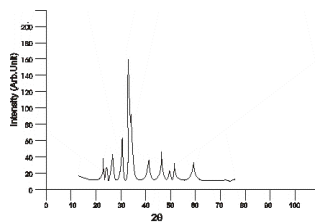
BaTiO₃ (Cat-A-SSR)



Ba_{0.93}Nd_{0.07}TiO₃ (Cat-B-SSR)

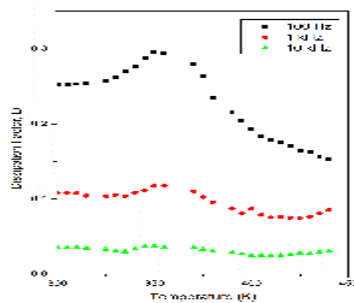
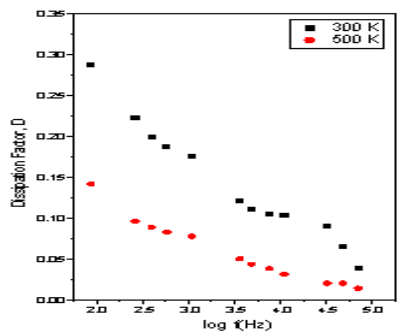
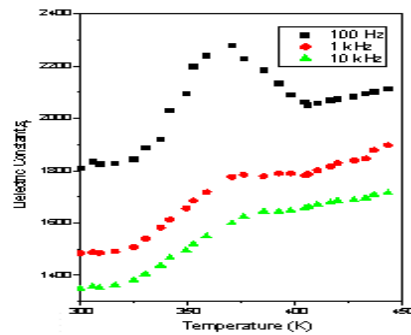
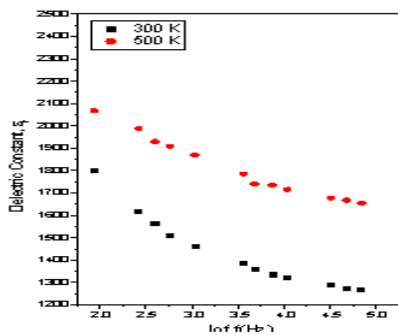


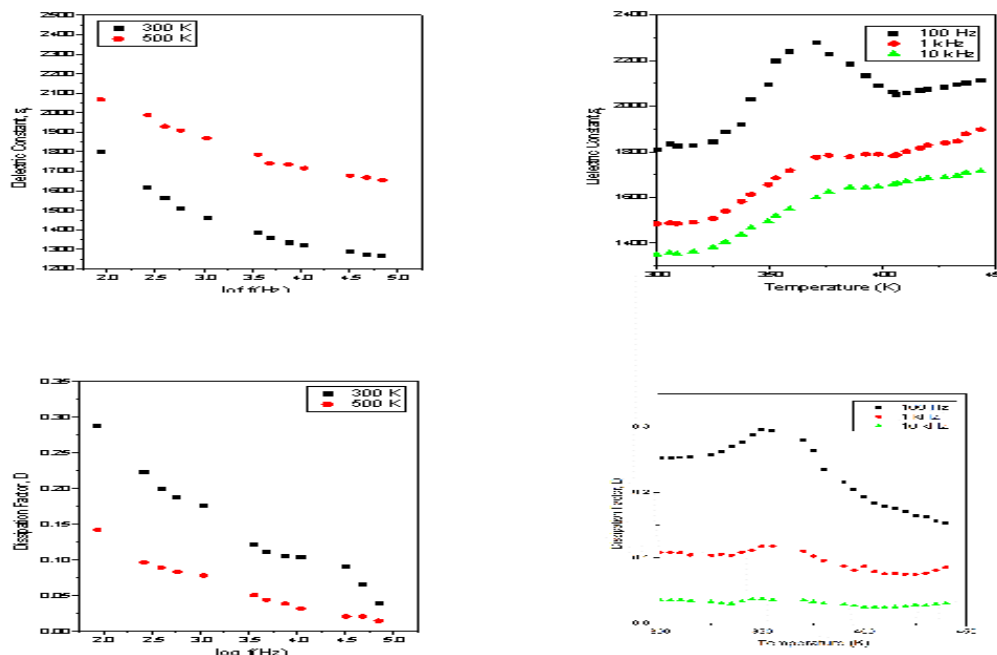
Nd_{0.70}Ba_{0.30}MnO₃ (Cat-C-SSR)



NdMnO₃ (Cat-D-SSR)

(Fig.I) Powder X-Ray Diffraction pattern for Different Catalysts





(Fig.II) LCR Studies Results:

SYNTHESIS OF CERAMIC-BASED CATALYSTS BY GREEN CHEMICAL METHOD

For the development of the alternative Green Chemical method following technique has been developed. A suspension of the required amount of different oxides and carbonate was prepared in Triton X-100 micellar medium. After leaving it for 2 h, the thick slurry was transferred into agate mortar and pestle for grinding. After mixing and grinding for 2 h, the powders were dried, ground for half an hour, and calcined in a covered high purity alumina crucible, and the mixture was further grinded for 1 h by the occasional addition of 2% w/w solution of polyvinyl alcohol (PVA) in Triton X-100. Thus produced powders were used for the preparation of different catalysts by general method, and the samples were then examined using X-ray diffraction to confirm the formation of single-phase materials.

All four catalysts, prepared by Green Chemical Method, have been written in this paper as follows:

1. BaTiO₃: Catalyst A-GCR
2. Ba_{0.93}Nd_{0.07}TiO₃: Catalyst B- GCR
3. Nd_{0.70}Ba_{0.30}MnO₃: Catalyst C- GCR
4. NdMnO₃: Catalyst D- GCR

TRANSESTERIFICATION

The transesterification process was used for the preparation of Biodiesel from Industrial waste oil. For this purpose calculated amount of sample of oil was collected in a 250 ml conical flask of borosil make. First of the entire oil sample was preheated on the hot plate with Magnetic Stirrer (Biocraft Scientific System Pvt .Ltd., India) at 600C for half an hour. A simultaneously calculated amount of methanol of

AR Grade was taken in a beaker, and the required amount of prepared ceramic catalyst was added into the beaker. Then the methanol and catalyst mixture was poured into the 250 ml conical flask containing the preheated oil. Heating was continued with magnetic stirring for 1 hour. After 1 hour, the reaction mixture was poured in a 500 ml Separating Funnel (J-Sil Make), and the reaction mixture was allowed to settle down for the separation of biodiesel from the glycerol layer for 24 hours. After it, there were exactly two layers separated in the separating funnel in which the upper clear layer was of Biodiesel, the Fatty Acid Methyl Ester of that particular oil, and the lower heavier layer was of glycerol. (Fig.III)

SEPARATION OF BIODIESEL:- After that, the lower glycerol layer was separated from the separating funnel for further process, as glycerol is a very useful by-product. The separation was done until both layers were separated completely. In some cases, the two layers were not separated properly, and then the entire mixture was resettled down overnight for the complete separation. So the both Biodiesel and Glycerol layers were separated for further test.

PURIFICATION OF PREPARED BIODIESEL: - The upper layer of Biodiesel was washed with hot distilled water 3-4 times until the clear layer was gained. Then the liquid was dried over dehydrating agents like anhydrous Calcium chloride. Glycerol was also separated by water washing. Now the Biodiesel sample was ready for further characterization and engine performance experiments.

By the use of the above procedure, Eight different sets of Biodiesel have been prepared, which are as-

1. IWO and NdMnO_3 – SSR catalyst
 2. IWO and NdMnO_3 – GCR catalyst
 3. IWO and BaTiO_3 – SSR catalyst
 4. IWO and BaTiO_3 – GCR catalyst
 5. IWO and $\text{Nd}_{0.70}\text{Ba}_{0.30}\text{MnO}_3$ – SSR catalyst
 6. IWO and $\text{Nd}_{0.70}\text{Ba}_{0.30}\text{MnO}_3$ – GCR catalyst
 7. IWO and $\text{Ba}_{0.93}\text{Nd}_{0.07}\text{TiO}_3$ – SSR catalyst
 8. IWO and $\text{Ba}_{0.93}\text{Nd}_{0.07}\text{TiO}_3$ – GCR catalyst
- (The Symbols SSR Catalyst and GCR Catalyst have been used for Solid State Route and Green Chemical Route, respectively)

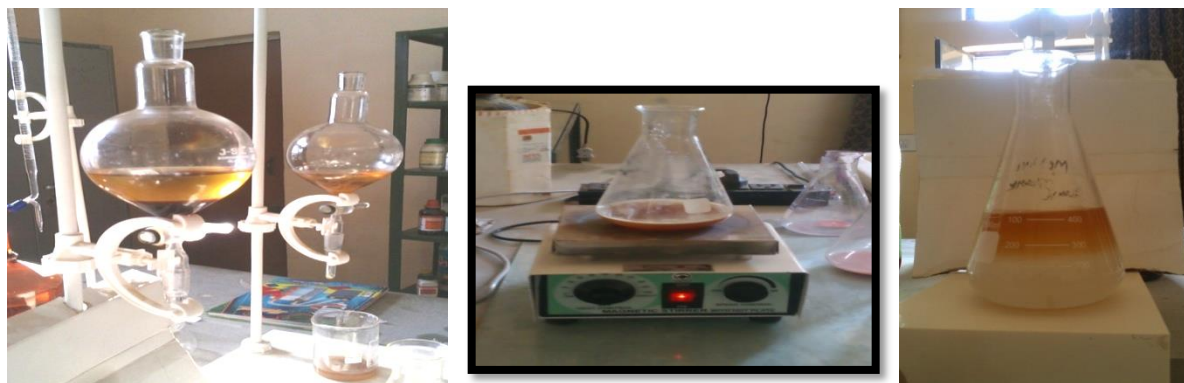


Fig. III: Transesterification process for Industrial Waste oil.

DETERMINATION OF PHYSICO-CHEMICAL PROPERTIES OF CONVENTIONAL DIESEL, NEAT INDUSTRIAL WASTE OILS, AND ALL EIGHT BIODIESEL SAMPLES

The general fuel-related properties like Viscosity, Kinematic Viscosity, Flash and Fire Point, Cloud & Pour Point, Density, Acid Value, etc., were determined as per standard methods and equipment as shown in Table 2.

Table 2. Physico Chemical Properties of Conventional Diesel, IWO-3 Oil, and its all biodiesel samples.

S.No	Properties	Unit	Diesel	IWO	-BD-Cat A (SSR)	-BD-Cat A (GCR)	-BD-Cat B (SSR)	-BD-Cat B (GCR)	-BD-Cat C (SSR)	-BD-Cat C (GCR)	-BD-Cat D (SSR)	-BD-Cat D (GCR)
1.	Flash Point	$^{\circ}\text{C}$	64 $^{\circ}\text{C}$	220	175	178	174	177	171	173	190	180
2.	Fire point	$^{\circ}\text{C}$	69 $^{\circ}\text{C}$	247	182	183	181	182	176	179	191	183
3.	Cloud Point	$^{\circ}\text{C}$	-7 $^{\circ}\text{C}$	8	6	3	5	2	3	2	5	2.5
4.	Pour Point	$^{\circ}\text{C}$	-11 $^{\circ}\text{C}$	0	-2	-3	-3	-4	-1	-2	0	-1
5.	Viscosity	Cst at 25 $^{\circ}\text{C}$	4.5	35.36	4.13	4.12	4.86	4.76	4.09	4.08	4.52	4.13
6.	Density	Kg/m^3	810	891	862	860	865	861	869	863	871	869
7.	Acid Value	mg KOH/g	0.78	0.86	0.80	0.71	0.48	0.76	0.14	0.10	0.41	0.38
8.	Iodine Value	g/100g	0.46	0.80	0.62	0.68	0.52	0.54	0.46	0.44	0.63	0.62
9.	Kinematic Viscosity	mm^2/S at 40 $^{\circ}\text{C}$	2.92	4.06	3.15	3.26	3.13	3.10	3.09	3.07	3.18	3.16
10.	Water Content	% by volume	0.03	0.04	0.06	0.07	0.04	0.03	0.02	0.03	0.05	0.03

DETERMINATION OF SPECTRAL PROPERTIES (ABSORPTION SPECTRA) OF ALL BIODIESEL SAMPLES

The UV spectra of all biodiesel samples of IWO have been taken by UV-Visible spectrophotometer (EC Double Beam UV-Visible spectrophotometer) and shown in Fig.IV.

The spectra of all biodiesel samples have been found comparable as per their original spectra.

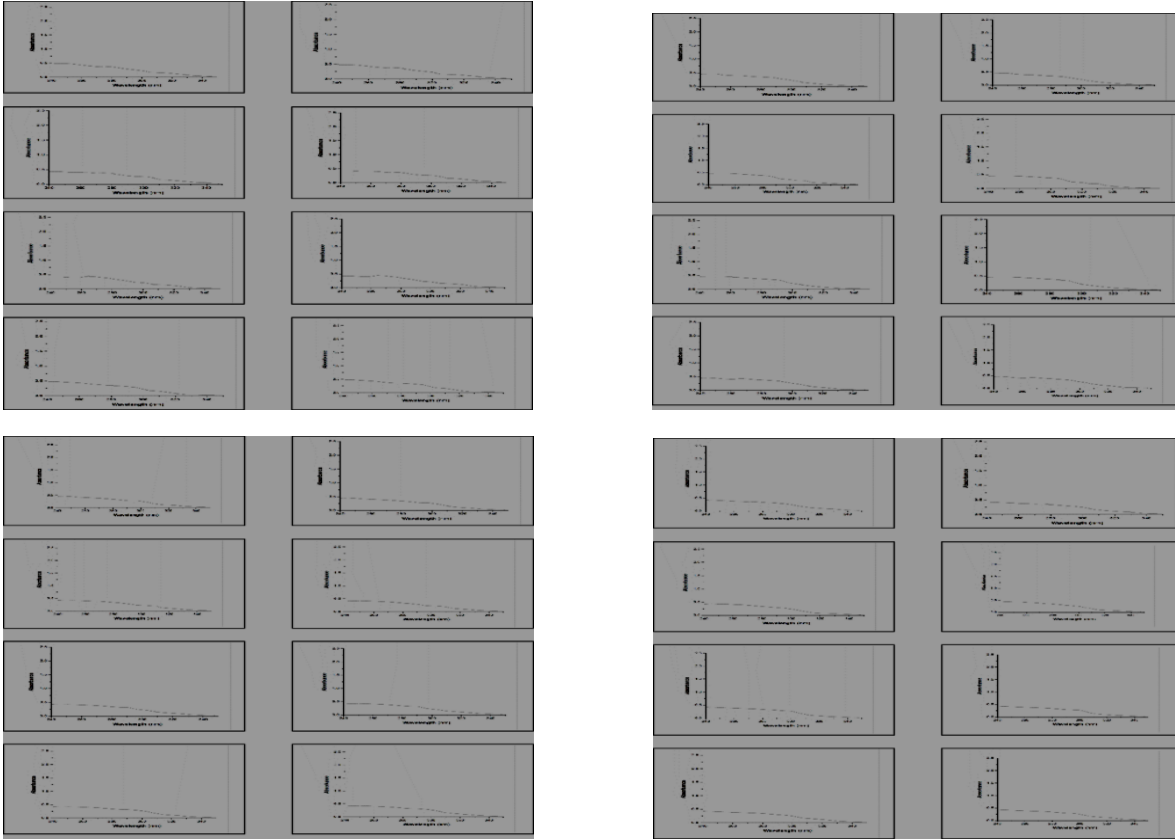


Fig. IV: Electronic spectra of eight biodiesel samples of Industrial Waste Oil

DETERMINATION OF ENGINE BASED PROPERTIES OF CONVENTIONAL DIESEL, NEAT INDUSTRIAL WASTE OIL, AND ALL EIGHT BIODIESEL SAMPLES

The Engine based properties of all biodiesel samples, conventional diesel, Industrial Waste Oil, have been calculated by virtue of the Computer Interfaced Variable Compression Ratio Multi-fuel Engine Test Bed (Legion Brothers, Bangalore). Fig.V



Fig.V: Interfaced Variable Compression Ratio Multi-fuel Engine (Legion Brothers Bangalore).

For all experiments, some optimized conditions were taken into consideration like blending 20%, Compression Ratio 18, Injection Needle Lift Pressure (bar) 203, injection time(°c A BTDC) 23, Engine Speed 1500, etc. The engine was stabilized before taking all measurements. The main three parameters, Brake Thermal Efficiency, Specific Brake Fuel Consumption, and Exhaust Analysis, were determined for all the samples as shown in Fig VI to X.

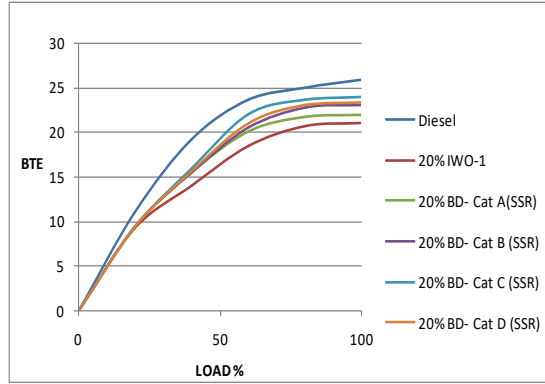


Fig.VI: Comparison of BTE of Diesel, IWO Oil-I, and its biodiesel samples prepared by SSR Catalysts

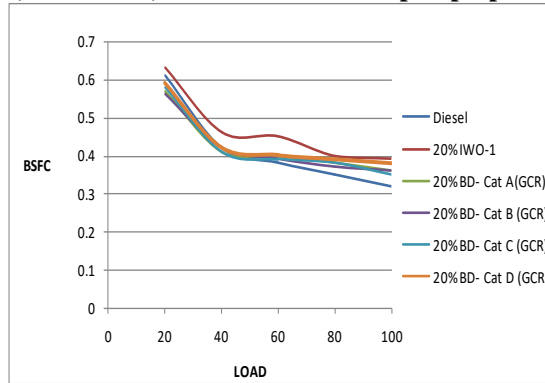


Fig.VII: Comparison of BSFC of Diesel, IWO Oil-I, and its biodiesel samples prepared by GCR Catalysts

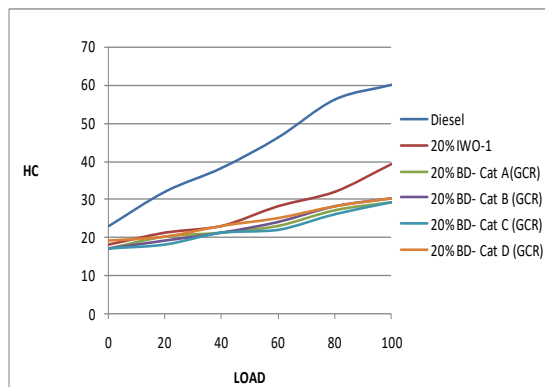


Fig.VIII: Comparison of HC Emissions of Diesel, IWO Oil-I and its biodiesel samples prepared by GCR Catalysts

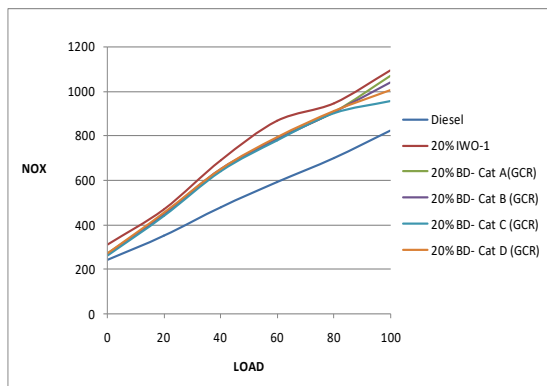


Fig. IX: Comparison of NOx Emissions of Diesel, IWO Oil-I and its biodiesel samples prepared by GCR Catalysts

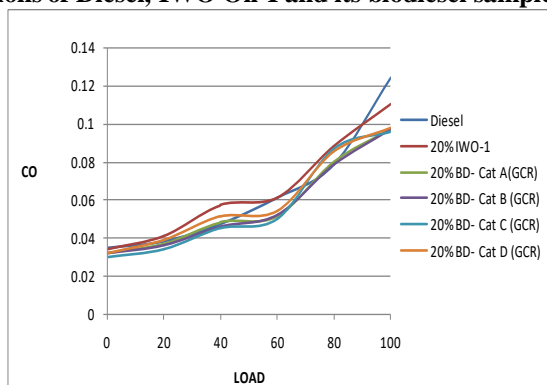


Fig.X: Comparison of CO Emissions of Diesel, IWO Oil-I and its biodiesel samples prepared by GCR Catalysts

Trace Metal Analysis:

Trace metal analysis on the entire sample, including Five nontransesterified IWO, was done by AAS and Spectroscopic Techniques (Table 4 and 5).

Biological Activity:

Biological Activity of the entire sample, including nontransesterified IWO against two bacteria E.Coli and S.Aures, has been performed.

Table 4: Determination of Zn (II) in different samples of Biodiesel prepared by Industrial Waste Oil.

S.No	Sample of Biodiesel	Zinc added	Zinc determined (µg/g)	% Recovery*
1	IWO-3.BD (Cat. A-SSR)	-	1.067	99.74
		0.10	1.164	
2	IWO-3.BD (Cat. A-GCR)	-	1.063	99.74
		0.10	1.160	
3	IWO-3.BD (Cat. B-SSR)	-	1.073	99.57
		0.10	1.168	
4	IWO-3.BD (Cat. B-GCR)	-	1.070	99.40
		0.10	1.163	
5	IWO-3.BD (Cat. C-SSR)	-	1.075	99.32
		0.10	1.167	
6	IWO-3.BD (Cat. C-GCR)	-	1.073	99.74

		0.10	1.170	
7	IWO-3.BD (Cat. D-SSR)	-	1.069	99.32
		0.10	1.161	
8	IWO-3.BD (Cat. D-GCR)	-	1.066	99.40
		0.10	1.159	

Table 5: Determination of Cu (II) in different samples of Biodiesel prepared by Industrial Waste Oil.

S.No	Sample of Biodiesel	Copper added	Copper determined (µg/g)	% Recovery*
1	IWO-3.BD (Cat. A-SSR)	-	1.364	99.80
		0.10	1.461	
2	IWO-3.BD (Cat. A-GCR)	-	1.359	99.79
		0.10	1.456	
3	IWO-3.BD (Cat. B-SSR)	-	1.371	99.80
		0.10	1.468	
4	IWO-3.BD (Cat. B-GCR)	-	1.367	99.59
		0.10	1.461	
5	IWO-3.BD (Cat. C-SSR)	-	1.376	99.73
		0.10	1.472	
6	IWO-3.BD (Cat. C-GCR)	-	1.374	99.73
		0.10	1.470	
7	IWO-3.BD (Cat. D-SSR)	-	1.366	99.80
		0.10	1.463	
8	IWO-3.BD (Cat. D-GCR)	-	1.364	99.59
		0.10	1.458	

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