Cerium Zirconium blended biodiesel

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Abstract

Our research work deals the effect of incremental injection pressure for 600bar in blended biodiesel (B30) -fueled in CRDI engine increases the performance (4.79%), decreases the emissions pollutants such as CO (16%), HC (9.52%) and Smoke(8.43%) except for NOX Compared to diesel(D100). The backup of the EGR system would reduce NOX emission(9.6%) in biodiesel (B30+15%EGR) and simultaneously increase other emissions. To overcome all these problems, novel cerium and zirconium oxide dual nano-additives blended biodiesel with EGR is used (B30+50CeO2+50ZrO2+15%EGR). The experimental results have shown that increasing injection pressure causes the reduction in ignition delay, integrate heat release rate and nano-additives enrich oxygen content for more engine performance characteristics such as an increase in BTE (11.27%) and decrease in SFC (14%) is observed. The combustion characteristics like inline cylinder pressure, heat release rate have developed, and emissions of CO (20%), HC (9.4%) and NOX (23.65%) have decreased thoroughly..

Keywords: *CRDI engine; EGR; Rice bran biodiesel; Nanoparticles; Engine performances; Emissions.*

1. Introduction

Worldwide the energy experts suggested that the demand of fossil fuel would be very high in future when compared with current scenario because of more consumption of fossil fuels in all sectors such as commercial, residential, industrial, power generation and transportation. Unavailability, increasing demand and concern with environmental pollution causes the need for the research in alternative fuel and it gives better performance and maximum reduction in emission-free greenhouse gases. It is efficient and effective than fossil fuels and the biodiesel is mainly one of the suitable alternative fuels which could be used efficiently in the diesel engine with no modification. The biodiesel fuel characteristics has a high viscosity, density, cetane number, and low calorific value compared to raw diesel. Various seeds such as rapeseed, sunflower, soya bean, Pongamia, curcus, jatropha, pinata, mango, cotton, peanut, karanji were used for the research of biodiesel and the engine performance of biodiesel was improved BTE, diminished SFC; diminished smoke, CO, and HC emissions but alternatively increased NO_X emission. It is observed combustion performance of biodiesel was increased engine cylinder pressure and net heat release rate compared to neat diesel. Thus biodiesel proved economically suitable fuel in the current energy scenario and also reduced harmful emission to the environment [27]. It is reported that aluminium oxide nanoparticles (50ppm and 100ppm) blended in Pongamia methyl esters (PME) are used in DI diesel engine. The sample fuels are B25, B25A50, B25A100.The AlO_2 nanoparticles blended biodiesel increased BTE and decreased SFC frequently, decreased the emission of smoke, CO and HC excluding for Nitrogen oxide emission which shows potential results in engine performance and reduction in emissions [23].

The investigation of mahua biodiesel blend in CRDI engine at a variable gasoline injection pressure increased from 22MPa to 88Mpa was studied, the maximum fuel injection pressure of 88MPa shows superior BTE and better combustion characteristics compared with additional injection pressures. Because of high fuel injection pressure, superior air-fuel mixture formation and well atomization, the emission of HC, Carbon monoxide and smoke were gradually decreased and unfortunately, NOx emission was increased [5]. An investigation made to the Calophylluminophyllum biodiesel blend with titanium oxide nanoparticles (40ppm) used in a single-cylinder engine with EGR the fuel samples test were conducted on diesel engine B20 and B2040TiO2 with and without 20% EGR. TiO_2 blended biodiesel with 20% EGR decreased (0.6%) BTE and increased SFC compared to the one without EGR, on the other hand, the oxides of nitrogen was increased when adding nanoparticles in biodiesel, sequentially using EGR the emission of NO_X were highly reduced. Thus it was observed that the EGR techniques reveal enhanced engine performance and reduced NO_X emissions [9]. The implemented analysis of the addition of nanoparticles cerium zirconium oxides (2.5ppm to 25ppm) in fuel as diesel there was no major change in properties and 31% reduction in smoke level as well as improved 3% BTE [6]. The fuel blends of biodiesel ethanol adding titanium nano additives results lowered BTE increased smoke, HC and NO_X emissions adding biodiesel ethanol to diethyl ether titanium and zirconium oxide particles improved release of heat rate and emissions due to lowered BSFC, smoke and NO_X the maximum reduction of emissions of smoke and Nitrogen oxide signified at the consequence of diethyl ether on low down-temperature ignition in CI engine [7].

The preparation of biodiesel using rice bran oil to methanol and nanocatalyst as calcium oxide from chicoreusbrunneus shell was done and properties of biodiesel were estimated and tests were conducted [28]. The parametric investigation of B20 Karanja oil in a CRDI engine particulate matter of toxicity measured using the benzene soluble natural division BSOF and ICP-OEM identified chemical component comparison and PM toxicity in fuel blends at different loading conditions. The peak of polycyclic aromatic hydrocarbons was carried out 60% of engine load at 1800 rpm and 20% load at 2400 rpm in CRDI engine [31]. The recognized study of spray characteristics and particulate size distribution at varying injection timing and injection pressure in the single-cylinder CRDI engine considered fueled as Karanja oil biodiesel blends and mineral oil blend thus concluded addition of biodiesel in test helped to reduce the particulate emission [35]. An experimental study was conducted for the performance and characteristic emissions by the fuel when biodiesel rice bran oil with diesel blend B20 is added with nano-additives cerium oxide (50ppm and 100ppm) respectively, thus it was finalized in a diesel engine that blended nano additives biodiesel results improved various properties and reduction in exhaust gas emission [36]. An experimental investigation was made by evaluation of performance and emission of CRDI engine fueled at different biodiesel blends, they were rapeseed diesel, methyl ester diesel and animal origin bio-fuel tested at steady-state parameters and it revealed comparison of results [37].

The production of biodiesel using baseline oil which is crude rice bran oil and catalyst KOH thus concluded the properties of RBO biodiesel similar to diesel and the tests SEM and energy dispersive x-ray were done for the sample of diesel and biodiesel collisions, results of performance and efficiency better than diesel and consequently higher in SFC slightly and emission showed decreased CO, HC and PM sequentially bit of increase in NO_X [38]. It is observed that matter of producing biodiesel from the raw materials rice bran oil and dewaxed degummed RBO below the critical temperature and pressure CO_2 was taken co-solvent to reduce the critical conditions of methanol the special effects were discussed quality and fatty acid yield, methyl esters were obtained 52% and 51% correspondingly while reacting with DD rice bran oil quality and yield gained 89 % and 94 % correspondingly and 16% of biodiesel were determined.[8]. The Jatropha biodiesel emission control strategy by adding aluminium and cerium nanoparticles 10ppm,30ppm and 60ppm, it was increased BTE compared to diesel and as per the conducted test result reduction in nitric oxide, carbon monoxide, hydrocarbon and smoke were 13%, 60%, 33% and 32% respectively [18].The blended fuel as n-pentanol with diesel and discussed its effect coupled with EGR the volumetric quantities of blends 10%-45% used in single cylinder DI engine at a constant speed, thus it concluded maximum reduction in NO_X when using EGR concurrently increased in CO and HC recognized.[11]. The optimization of rice bran biodiesel with diesel production catalyst used NaOH with certain quantity. Thus blended biodiesel fuel properties, characteristics, efficiency and emission were better than diesel so that it was recommended for the CI engine [10].

The sample blends rice bran with diesel different volumes of percentage at different injection pressures whereas 220bar considers for a review decreased in emission and smoke The injection pressure and the parameter influenced the high combustion rates that result in minimizing smoke and emission. [12]. A comparison study of waste cooking oil biodiesel and commercial diesel for the effect of injection parameter on combustion characteristics were made. The common rail direct ignition tested pressures were 80 and 160 MPa, crank angle injection timing found -25 and 0-degree peak biodiesel cylinder pressure and peak heat release rate slightly lowered ignition delay longer under the operating conditions when using biodiesel NO_X emission higher than the diesel rest of emissions reduction in high injection pressure [32]. The mahua biodiesel blend with aluminium oxide nanoparticles was used to inspect the effect of fuel performance, characteristics in CRDI engine and the aluminium oxide were spherical shaped particle it was confirmed by scanning electron microscopy. Nanoparticles added in equal proportions in the blend of fuel mahua methyl biodiesel MME20 using ultrasonicator cetyltrimethylammonium bromide as a cationic surfactant for suspended nanoparticle nanofluid preparation the fuel was a maintainable enhancement in BTE and peripheral reduction in emission [34]. The rapeseed methyl ester biodiesel with organic base manganese additives was used for the investigation of combustion and emission characteristics. When adding the nano-additives, calorific value increases and atomization of fuel increases. Enrichment in fuel characteristics and combustion the results of emission reduction was CO 25.5%, HC 6.64%, smoke 6.5% and NO_X 25.52% [20].

The parameters of in-line pressure and temperature, mass fraction burned (MFB), knock limited maximum brake torque (KLMT 8 crank angle at 7.0 bar IMPE and ISFC net reduced by 4.1%) in the direct injection spark ignition (DISI) engine at various loads between 5.5 bar and 8.5 bar that identified IMPE with various EGR ratios up to 13% [13]. The rice bran oil production by using ethanol blend for performance and combustion characteristics with different quantities was studied [14]. The mangos seeds are transformed into methyl esters through the process of transesterification to reduce viscosity and high volatility. The objectives of their study were to improve performance and combustion characteristics in a Kirloskar diesel engine of methyl esters and mango seed biodiesel to diesel. Different fuel proportions were conducted in test and it differentiated by BTE, SFC, smoke and emission [4]. The n-butanol blend with diesel was prepared for combustion and emission characteristics the fuel blend sample as 40% n-butanol to diesel the samples used to run the heavy-duty diesel engine embedded EGR at constant speed 1400 rpm and 1.0 bar IMEP. The B40 gave the long ignition delay but higher NO_X to overcome this EGR is used NO_X reduced due to lower soot the same process repeated by changing fuel blend ratio that result was observed Ultra-low NO_X and soot emission gradually high thermal efficiency level maintained [15]. The jojoba oil was used to produce the jojoba methyl ester blended diesel and adding multi-walled carbon nanotubes for the impact on better combustion performance and emission characteristics. They were involved in Fourier Transform infrared test, Gas chromatography-mass spectrometry, SEM and TEM tests. It was taken out the result of the peak pressure release rate and heat release rate were increased at 7%,4% and 4% respectively, MWCNTs-B20D, MWCNTs-JB20D and JB20D samples were tested then MNCNTs was recommended for significant improvement in JB20D [1].

The above literature studies explained the details of the biodiesel requirement, qualitative properties, performance, combustion characteristics, emission control methods and strategies that were used in adding nano-additives. The addition of nano-additives plays a very important role in fuel enrichment and also EGR technique is used to minimize the emission levels. In our research work, the objectives explain the effect of CRDI Engine; brake thermal efficiency, net heat release rate, and specific fuel consumption and emission control in enriching properties of selected novel modern rice bran oil biodiesel by addition of cerium-zirconium oxide. CeO_2 reduces CO, HC and NO_X emission and slightly develops the combustion characteristics in the premixed phase but ZrO_2 releases a higher heat release rate that reveals better combustion and nominal reduction in emissions compared to CeO_2. The higher concentration of nano additives (more than 100 ppm) blended with biodiesel leads to lack of stability and poor suspension quality of nanoparticle in biodiesel and hence, the novel optimal mixed (50 ppm CeO_2+50 ppm ZrO_2) nano additives blended biodiesel is used as a fuel for this experimental work.

2. Biodiesel and nano fuel production and testing method

Biodiesel could be produced from a number of the process such as chemical reactions, transesterification process and esterification. Among them, the transesterification process is considered the most advantageous and economical method for the production of biodiesel. Fig. 1 shows the transesterification process conversion of oil to biodiesel in the presence of a few catalytic reagents and alcohol as the report of [16].

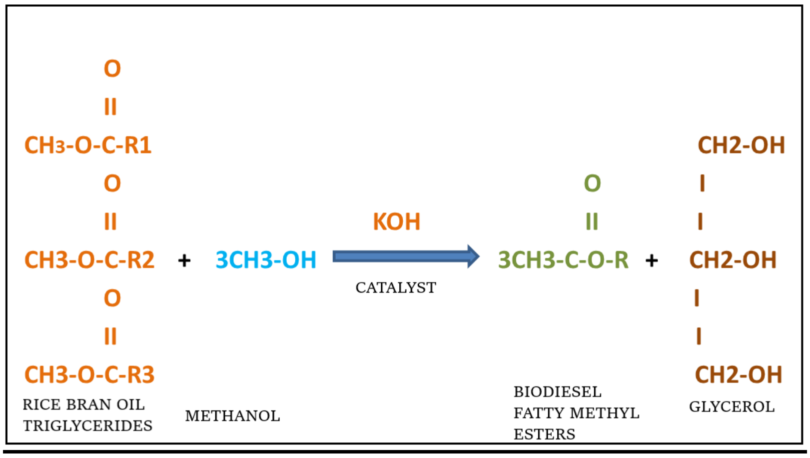


Fig. 1 Chemical reaction of the transesterification process of rice bran biodiesel

Transesterification process stoichiometrically could be completed by maintaining the molar ratio 3:1 of alcohol to triglycerides. In transesterification, acid could be used as base-catalyzed but mostly base-catalyzed being used for the production of biodiesel. The rice bran oil is readily extracted from the suitable process and a fuel property of the crude oil is tested. The nano fuel preparation method and setup are as shown in Fig. 2.

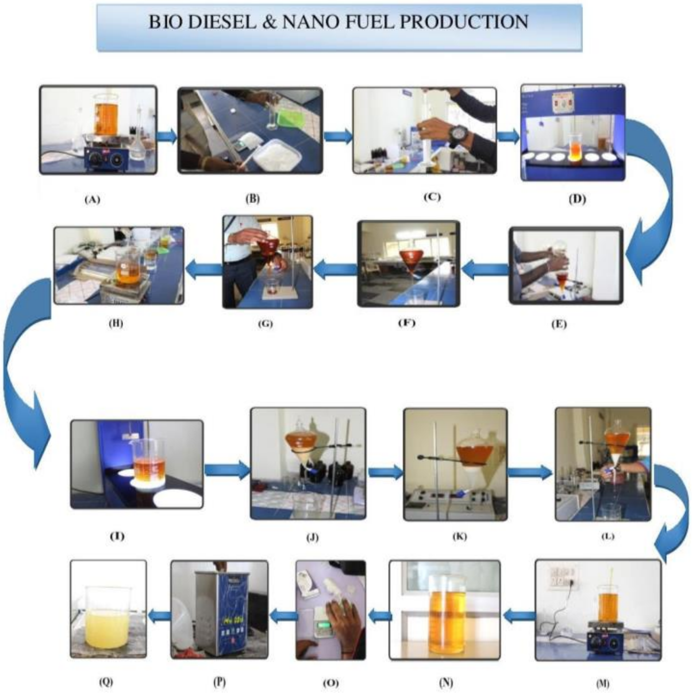


Fig. 2 Biodiesel and nano fuel production method

The Rice bran oil is taken in a separate glass beaker of quantity 1000 ml and it is heated with an electric induction heater. The ratio of methanol and oil is 0.2:1 with catalyst KOH as 0.5% to1% to the volume of oil adding each other subsequently. The required reaction temperature is 50°C-60°C and the stirring rate is 300-700 rpm for the reaction time of 50-90 minutes. During this process, the triglycerides are separated from the oil. After the required time the mixture is poured into the separatory funnel and kept for the settling of glycerol. This is due to the density difference between glycerol and biodiesel. The glycerol is deposited in the bottom of the funnel and crude biodiesel is at the top within the settling period of 24 hours. The glycerol is separated by an opening through the valve screw and is stored in a separate container. The crude biodiesel is then removed from the funnel and taken in the glass container than that resulted in maximum biodiesel yield of 95.3% are followed. The biodiesel contains a higher amount of impurities, this could be removed by treating the biodiesel with water. The ratio of water and biodiesel is 0.2:1 where water is heated up to the temperature of 40°C and it is added to the crude biodiesel. Again the mixture is kept at the magnetic stirrer for 15 minutes. Then the mixture is kept for about 8 hrs in the separation funnel. After the process, the soap oil and the water mixture are deposited at the bottom of the funnel. The colour of the mixture is milky white and this consists of some quantity of glycerol. After the separation of water from the funnel, the biodiesel is taken in a separate glass beaker and heated about 100°C – 120°C to evaporate the excess water finally, the pure biodiesel is obtained [17]. In addition, the nano-additives of cerium and zirconium oxides are considered to be used as a fuel-borne catalyst for biodiesel to improve engine performance [2]. The nano additives are used in powder form and the particle size is 20 nm to 30 nm and specifications of nanoparticles are represented in Table 1, purchased from a nano research lab at Jharkhand. The sample fuel of 1000ml of biodiesel is mixed with the 50 ppm of cerium oxide and 50 ppm of the zirconium oxide nanoparticles with 5% of the oleic acid is added in ultrasonicator. The process takes place around 1 hr to the complete blending of the fuel.

Table 1: Properties of nanoparticles

PROPERTIES	DESCRIPTION	
	Cerium oxide(CeO_2)	**Zirconium oxide(ZrO_2)**
CAS NO	1306-38-3	1314-23-4
Color	Light yellow	White
Density	6.5 g/cm^3	5680 kg/m^3
Particle size	20-30nm	30-50 nm
Boiling point	3500^{o}C	4300^{o}C
FTIR wave range	400-4000cm^{-1}	355-285 cm^{-1}
Atomic weight	172.114 g/mol	231.891 g/mol
Purity	99.7%	99.9%
Melting point	2600^{o}C	2715°C
Crystallographic structure	Spherical	Spherical

The surfactant is formed a layer over the nanoparticles avoiding the deposition of the particles in the fuel tank since the nanoparticles spread widely which lowers the surface tension between the liquid and solid phases there is repulsive force act in the concern particles hence it could not able to reach the bottom of the tank because of zeta potential principle, this increases the stability of the particles. The small size of spherical particles sedimentation velocity in a liquid is measured by stroke law.

$$V = \frac{2R^2}{9\mu}\left(\rho_P - \rho_L\right).g \tag{1}$$

Whereas V denotes sedimentation velocity of the particle, R is the radius of the particle, µ is the viscosity of the liquid, p_P and p_L are their particles and liquid densities, and g is the gravity of acceleration. Consistent with the equation (1) the nano-sized particles might be improved stability and reduced the terminal velocity as the known speed of particles while sedimentation in base fuel. Oleic acid is primarily used as the surfactant having 7.45pH which comes under carboxylates belongs to anion structure of the negative hydrophilic head and a long hydrophobic tail, therefore, outer negative hydrophilic head maintains suspension to others, and the layer ignores particles accumulation and prevents the deposition. The ultrasonication is the process of diffusing nanoparticles in the blended biodiesel, hereafter nanoparticles are equally dispersed in biodiesel with an ultrasonic frequency of the agitation around the range of 40-60 kHz with the ultrasonic power of 120W.

2.1 Free Fatty Acid Profile

The impulsive level of Free fatty acid of rice bran oil and rice bran biodiesel were fixed with aid of gas chromatography (GC) analyzer which is the process of sampler fluid where held in oven, Flame Ionization Detector (FID) and Nitrogen gas carrier together with GC, the composition of the Free Fatty Acids in oil and biodiesel has denoted total saturated fats 17.892%, 18.849% and total unsaturated fats 82.102%, 81.152%. Therefore unprompted fatty acid composition briefly mention in table percentage-wise, so far the discussion of free fatty acids that realized here C:D let it denotes the C represents number of carbon atoms and D is number of double bonds carbon atoms chain, oleic acid C18:1 having volumes of 42.013%, 41.414% respectively in oil and biodiesel, it have singular characteristics of emulsify agent so that it could sustain the structure of chemical compounds and solubilize in other blends and which is used also surfactant to avoid agglomeration of nanoparticles while dispersing in biodiesel, alike linoleic acid C18:2 swift drying characteristics it could be relevant oxygenation in air they are 38.236%, 38.032% in oil and biodiesel, palmitic acid C16:0 which is act as release agent in biodiesel and it routes to increase the volatility the volume 14.883%, 15.897% contained respectively in oil and biodiesel, other acids such as Linolenic acid C18:3 is 1.396% and 1.401%, Stearic acid C18.0 have 1.297% and 1.281% were focused on the main acids in rice bran biodiesel [30]. The fuel properties are tabulated in Table 2.

Table 2: Fatty Acid Profile of Rice Bran Oil (RBO) and Rice Bran biodiesel (RBD).

Acid	Type	Form	RBO	RBD
Oleic	Unsaturated n-9	C18:1	42.013	41.414
Myristic	Saturated	C14:0	0.122	0.069
Margaric	Saturated	C17:0	0.029	0.018
Linoleic	Unsaturated n-6	C18:2	38.236	38.032
Linolenic	Unsaturated n-3	C18:3	1.396	1.401
Palmitoleic	Unsaturated n-7	C16:1	0.142	0.1007
Palmitic	Saturated	C16:0	14.883	15.897
Behenic	Saturated	C22:2	0.576	0.623
Lignoceric	Saturated	C24:0	0.226	0.192
Erucic	Unsaturated	C22:1	0.036	0.027
Arachidic	Saturated	C20:0	0.759	0.769
Arachindonic	Unsaturated n-6	C20:4	0.252	0.178
Stearic	Saturated	C18.0	1.297	1.281
	Total Saturation		17.892	18.849
	Total unsaturation		82.102	81.152

2.2 Analysis of Fuel Properties

The samples of biodiesel and nano additive blended biodiesel such as rice bran crude oil, rice bran biodiesel, B30, B30+50CeO_2, B30+50ZrO_2, B30+50CeO_2+50ZrO_2 are tested for the various properties as density, cetane number, calorific value, fire point, flash point and are compared to diesel as per ASTM blend standards and their effects are recognized. The nano additive blended biodiesel of B30+50CeO_2+50ZrO_2 has similar to the diesel fuel properties compared than other blends. The fuel properties are tabulated in Table 3.

Table 3: Fuel properties comparison of diesel, biodiesel and nano fuel

Fuel properties	ASTM Standards	D100	Rice bran oil	Rice bran biodiesel	B30	B30+50 CeO_2	B30+50 ZrO_2	B30+50 CeO_2 +50 ZrO_2
Density at 20^0C(kg/$m^{3)}$	D 1298	820	960	868	846	831	835	824
Kinematic viscosity at 40^0C(mm^2/s)	D 445	2.72	30.26	5.03	3.47	3.14	3.19	2.92
Flash point (^{0}C)	D 93	56	210	165	78	62	65	60
Fire point (^{0}C)	D 93	62	242	182	81	70	72	68
Calorific value(kJ/kg)	D 240	45000	36283	39454	42886	43987	43732	44198
Cetane number	D 613	48	42	57	49	51	50	53

Fourier Transform Infrared Spectroscopy is an analysis technique which is used to determine the vibrational motion of functional groups present in the samples of diesel; methyl ester diesel blend B30 as shown in Fig. 3 and methyl ester diesel blends B100 as shown in Fig. 4. The spectrum band generates that absorption frequencies in the infrared region while distributed light rays (IR-Infrared rays) on the sample through interferometer and beam splitter the peaks identifies from the spectrum band that the peak is nothing but absorbents of vibration molecules of functional groups and its concentration of the mixture. The investigation apparatus has MIR [Mid-range] between 400 cm^{-1} and 4000 cm^{-1} and 1cm^{-1} resolution the spectrometric graph between transmittance and IR frequency range they are measured in wavelength and wavenumbers in cm^{-1}. In our research work sample, rice bran methyl ester blend B30 has high peaks as shown in Fig. 3 and clearly tabulated at 2955 cm^{-1}to 2855cm^{-1} in Table 4.

Table 4: FTIR analysis of B30

Frequency of FTIR Range (Cm^{-1})	Family	Chemical Bonds
2855-2955	Alkanes	C-H Stretching
1745.26	Ester/Aldehydes	C=O Stretching
1461.78	Alkanes	-C-H Bending
723.175	Alkanes	=C-H Bending

The double bond stretching vibration related to C-H Alkyl methylene group which frame olefin and to extend fluctuation and reduce at methyl group and the second peak clearly at 1745 cm^{-1} C=O carbonyl group it frames esters the C-H group's tendency in -CH_3 and CH_2 assignment and as same as the B100 sample as shown in Fig. 4. In between 3007cm^{-1}to 2926 cm^{-1}stretch combined with 2855 cm^{-1}and yield stretch has shown -CH_2 and the C-H alkyl group is present at another peak got at 1743 cm^{-1} carbonyl C=O aldehyde are identified both sample bending has approximately at 723 cm^{-1}. The sample of Diesel is shown in Fig. 5 have similar functional groups at the approximate region of wavenumber in the spectrometric image, the appropriate values were given as well as the functional group families and type of vibration motion are tabulated in Table 5.

Table 5: FTIR analysis of diesel and B100

Diesel			Rice bran methyl ester Biodiesel (B100)		
Frequency of FTIR Range (Cm^{-1})	Family	Chemical Bonds	Frequency of FTIR Range (Cm^{-1})	Family	Chemical Bonds
2855-2924	Alkanes	C-H Stretching	2855-2926	Alkanes	C-H Stretching
1461.78	Alkanes	C-H Bending	1743.33	Aldehydes	C=O Stretching
1376.93	Fluoride	C-X	1462-1438	Alkanes	C-H

					Bending
723.17	Alkanes	=C-H Bending	723.175	Alkanes	=C-H Out of plane Bending

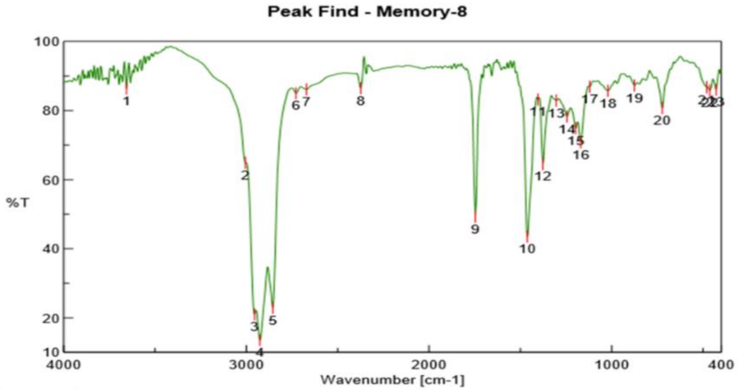
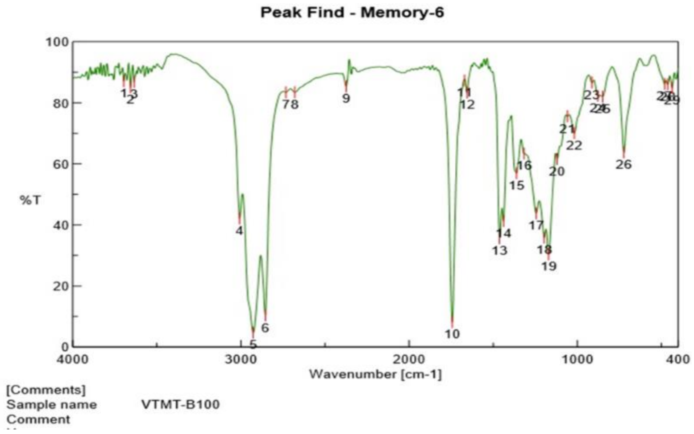


Fig. 3 FTIR analysis in the spectrum of B30



[Comments]
Sample name VTMT-B100
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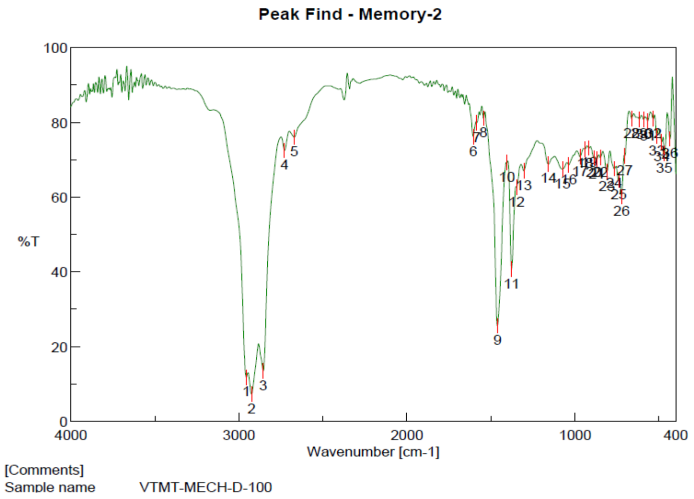
Fig. 4 FTIR analysis in the spectrum of B100



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Sample name VTMT-MECH-D-100

Fig. 5 FTIR analysis in the spectrum of D100

Conversely the shape and size of cerium oxide and zirconium oxide nanoparticles morphologies are taken individually through the help of scanning electron microscope ZEISS and the parameters as true working distance are 8.1 mm, EHT range 10.00Kv for the specimen length 100nm and magnification range 200KX.

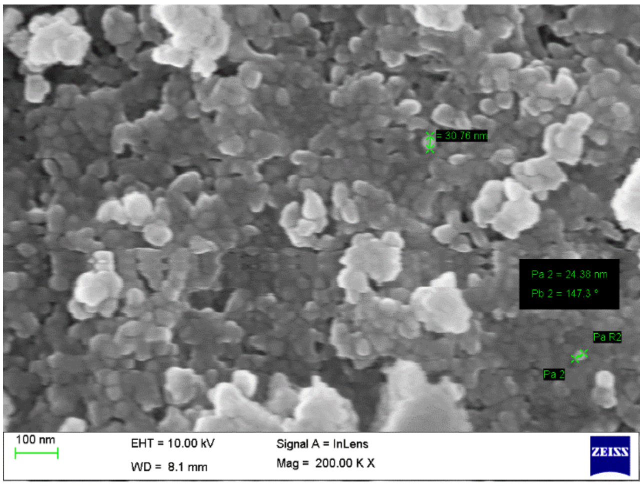

Fig. 6 SEM test images of CeO_2 nanoparticles

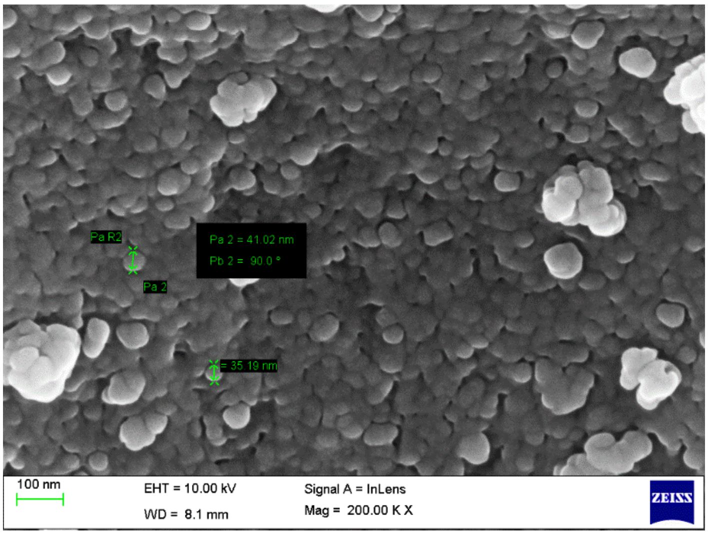

Fig. 7 SEM test images of ZrO_2 nanoparticles

It is characterized by spherical shape microstructure for both cerium oxide and zirconium oxide and particle diameters are differs for CeO_2 24.38 nm - 30.76 nm at 147.3° as shown in Fig. 6 and for ZrO_2 35.19 nm -41.02 nm at 90° as shown in Fig. 7.

3. Test Engine and Experimental Procedure

3.1 CRDI Engine Set up

The engine setup utilized in this research work is CRDI common rail direct injection system. The nano additive blended biodiesel is used as a fuel in this engine with some specific quantity. CRDI engine gives superior performance when compared with the usual engine due to its high fuel injection pressure leads to the complete atomization of the fuel [3]. Furthermore, due to its proper timing, complete combustion of the fuel takes place which reduces the emission of unburnt particulates and increasing the engine performance. This setup consists of a single-cylinder, four strokes, CRDI engine with power 3.5 kW at 1500 rpm is connected to eddy current dynamometer. The capacity of the engine is 661cc and compression ratio 17.5:1. It turns in supply with important devices for the crank angle, cylinder pressure, the flow of fuel, the flow of air, load and temperature measurements. Those signals are interfaced to the PC via the excessive-speed data acquisition device. The installation has stand-on panel box together with twin fuel tank, airbox, manometer, transmitters for air and gas drift measurements, gasoline measuring unit, process indicator and piezo power unit. The Rotometer supply engine cooling water with flow dimension. CRDI engine works with programmable open ECU for diesel injection, gasoline injector and common rail with the rail pressure sensor and cranks location sensor, pressure variable control device, a gasoline pump and wiring harness. The engine is monitoring with soft lab view and record the online engine performance as well as combustion characteristics. The experimental CRDI engine setup is shown in Fig. 8 and the specifications are tabulated in Table 6.

Table 6: Specifications of CRDI engine setup

Engine parameter	Specification
Product	CRDI VCR Engine
Engine make	Kirloskar, Single cylinder, 4 stroke.
Category of cooling and ignition system	water cooled and CI
brake power	3.5 KW at 1500 rpm
Bore x stroke, displacement	87.5 x 110 mm, 661cc
Injection pressure	200-800 bar
Injection timing	23obTDC
Number of nozzle hole and diameter	3 holes and 0.3mm
Compression ratio	17.5:1
Types of the combustion chamber	Hemispherical
Dynamometer	Eddy current type, water cooled with the loading unit
ECU	Model Nira i7r with programmable ECU software
EGR	Water cooled
Data acquisition device	NI USB-6210, 16-bit, 250kS/s.

The engine exhaust emissions such as CO, HC, CO_2, O_2, and NO_X are measured and recorded by AVL DI gas 444N (five gas analyzer) and another emission of smoke is measured by AVL 437 smoke meter. The emissions measuring instruments range and resolution are tabulated in Table 7.

Table 7: The measurement accuracy and resolution of exhaust five gas analyzer and smoke meter

Measurement data	Resolutions
HC – 0-20000ppm Volume	1ppm/10ppm
CO – 0-15% Volume	0.0001% Volume
CO_2 – 0-20% Volume	0.1% Volume
NO_x– 0-6000ppm Volume	1ppm Volume
O_2 – 0-25% Volume	0.01% Volume
Opacity – 0-100%	0.1%
Absorption (K Value)	0-99-99m^{-1} 0.01m^{-1}
Measurement data	Resolutions
HC – 0-20000ppm Volume	1ppm/10ppm
CO – 0-15% Volume	0.0001% Volume
CO_2 – 0-20% Volume	0.1% Volume
NO_x– 0-6000ppm Volume	1ppm Volume
O_2 – 0-25% Volume	0.01% Volume
Opacity – 0-100%	0.1%
Absorption (K Value)	0-99-99m^{-1} 0.01m^{-1}

The experimental tests are conducted at constant compression ratio 17.5:1 and different load conditions (0%, 25%, 50%, 75%, and 100%). The engine experimental results are carried out more times and then averaged when the engine reaches under steady-state conditions.

3.2 EGR

The EGR set up is shown in Fig.8.

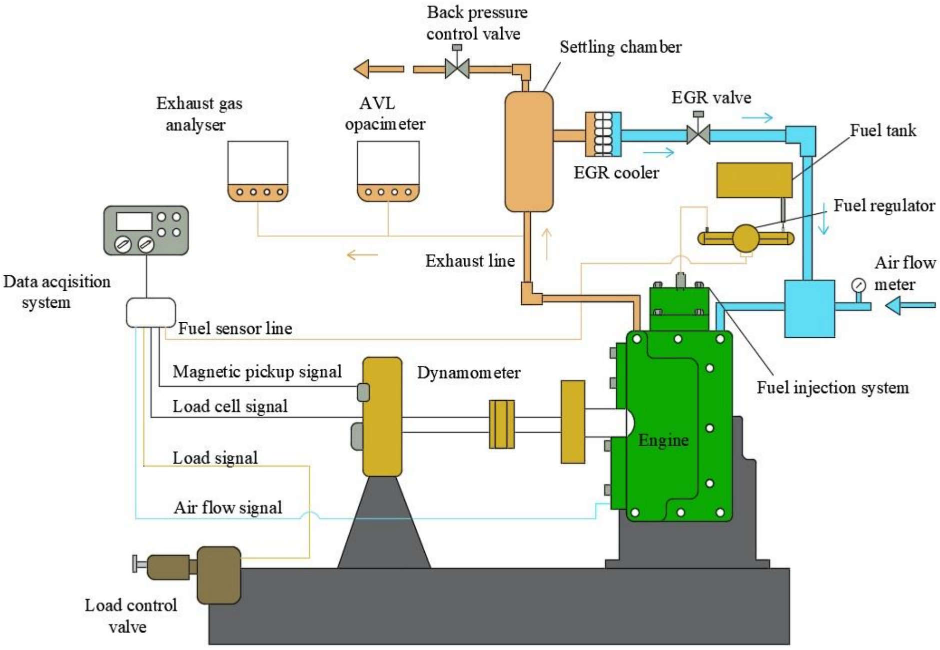

Fig. 8 CRDI Engine experimental setup

It is a supplementary component and is attached with engine exhaust to reduce the NO_X emission from the engine. EGR works by recirculation of some portion of exhaust gas from the engine and it returns to the combustion chamber through the inlet manifold [24]. The EGR percentages were measured by the intake and exhaust of CO_2 Concentration, the percentage of EGR are taken in equation (2).

$$\%EGR = \frac{(CO_2)intake}{(CO_2)exhaust} X100 \tag{2}$$

This unburnt gas dissolves in O_2 of the inlet air and provides gases into the combustion chamber thereby decreasing the inline cylinder pressure and the temperature. NO_X is produced in high cylinder temperatures and pressures hence it should be reduced. In a diesel engine, the exhaust gas substitutes the oxygen presents in the fuel mixture because NO_X forms mainly when a mixture of chemical reaction nitrogen and oxygen gas molecules at a high temperature. By lowering the temperature of the combustion chamber by the EGR it restricts the formation of NO_X. EGR could be used at 5%, 10%, 15% and 20%; higher percentage of EGR could readily increase all the emission except the NO_X and also reduces the engine performance and low quantity fraction of EGR would not show major changes in NO_X emission, Therefore 15% of the EGR is used in the engine systems [19].

4. Result and Discussion

The experimental results of the engine performance, combustion characteristics and emissions are carried out in the CRDI engine at maximum load conditions with constant rpm and constant compression ratio. The engine performance of brake thermal efficiency, Specific fuel consumption, the combustion characteristics of cylinder pressure, heat release rate, the emissions of smoke, CO, NO_X and HC are investigated in this research work.

4.1 Performance Characteristics

4.1.1 Brake Thermal Efficiency

BTE is calculated as the ratio of energy generated in the brake power to the input energy of mass of fuel per second and calorific value of fuel. This is one of the important parameters in the performance of the engine. The variation of brake thermal efficiency with respect to load at the constant injection pressure of 600 bar for different fuel blends, such as D100, B30, B30+15%EGR, B30+50CeO_2+15%EGR, B30+50ZrO_2+15%EGR, B30+50CeO_2+50ZrO_2+15%EGR are shown in Fig. 9.

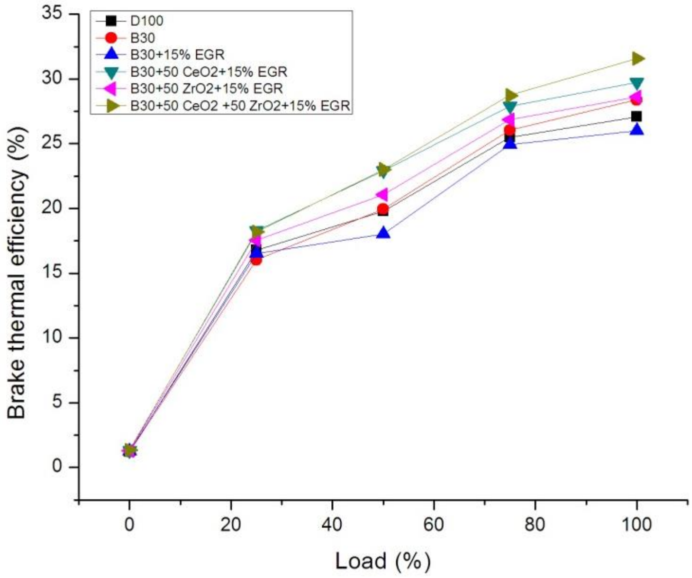

Fig. 9 Variation of BTE with respect to load for different fuel blends

The experimental tests are conducted with and without a load in the CRDI engine that the loads are applied gradually, hence it varied from 0 to 100% for all the fuel samples. It is observed that due to increasing the load, the BTE increased on account of increasing engine cylinder wall temperature [21, 26]. Biodiesel fuel properties have after transesterification process is similar to diesel. Biodiesel (B30) has released higher brake thermal efficiency when compared to diesel (D100) as a result of biodiesel gives better lubricity, higher cetane number. It has been claimed more complete combustion hence increasing the thermal efficiency. The brake thermal efficiency was unexpectedly losing with the EGR applied for biodiesel (B30+15%EGR), due to the reason of exhaust gas recirculation into the combustion chamber leads to dropping the ignition rate of fuel. Dual nanoparticle blended biodiesel fuel with EGR, B30+50CeO_2+50ZrO_2+15% EGR is higher BTE (31.59%) compared to all other fuels such as B30+50CeO_2+15%EGR (29.75%), B30+50ZrO_2+15%EGR (29.62%), B30 (29.39%), due to the reason of increasing the quantity of nano additives dosage (100ppm) in biodiesel blends promotes highly chemical reactivity and rapid swirl combustion which leads to a considerable improvement in combustion and dual nanoparticles (CeO_2+ ZrO_2) blended biodiesel released the higher concentration of oxygen for the duration of combustion so that nano fuel combustion reveal better BTE. The lower BTE (26.91%) is observed in B30+15%EGR

4.1.2 Specific Fuel Consumption

SFC is fuel consumed per unit time to the engine power. This parameter is inversely proportional to the brake thermal efficiency. Variation of SFC with respect to load for different fuel blends at a constant injection pressure of 600bar is shown in Fig. 10.

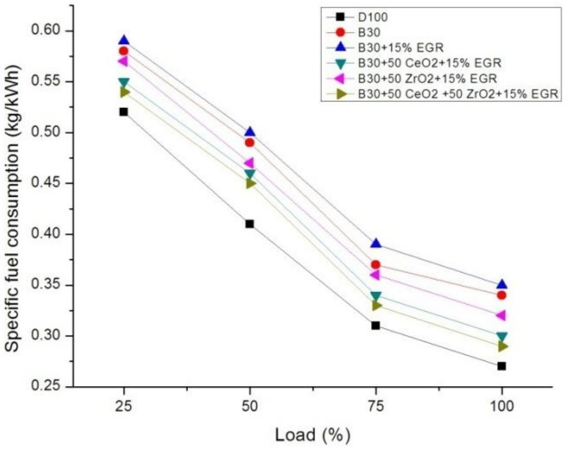

Fig. 10 Variation of SFC with respect to load for different fuel blends

In this research work, the specific fuel consumption of B30 blends gave 0.34 kg/kWh is higher than the Diesel was 0.27 kg/kWh as a result of lower calorific value, higher viscosity and higher latent heat vaporization of biodiesel blends than diesel. In the accumulation of nanoparticle blended biodiesel with EGR, B30+50CeO_2+15%EGR was 0.30 kg/kWh and B30+50ZrO_2+15%EGR was 0.32 kg/kWh consumed slightly lower than the B30, as well as mixed nanoparticles of B30+50CeO_2+50ZrO_2+15%EGR, gave 0.29 kg/kWh also have very low fuel consumption other than all fuel blends because of the higher surface to volume ratio improved the combination rate of air and fuel and increases the oxygen content in nanoparticles and one more reason an addition of increasing dosing level of various nanoparticles in biodiesel blends reacts the decreasing fuel flow resistance that improves proper atomization and fuel vaporization which leads to the reduction of fuel consumption [22]. With using of EGR in biodiesel blends B30 gave 0.35 kg/kWh is very higher comparing with all other fuel blends due to the recirculation of unburned exhaust gas into the intake manifold of the combustion chamber and insufficient oxygen level.

4.2 Emission Characteristics

4.2.1 CO Emissions

Due to inadequate oxygen in the fuel during the combustion progression promotes CO emissions. The maximum CO emission is generated when an engine runs at full load conditions. Fig.11.

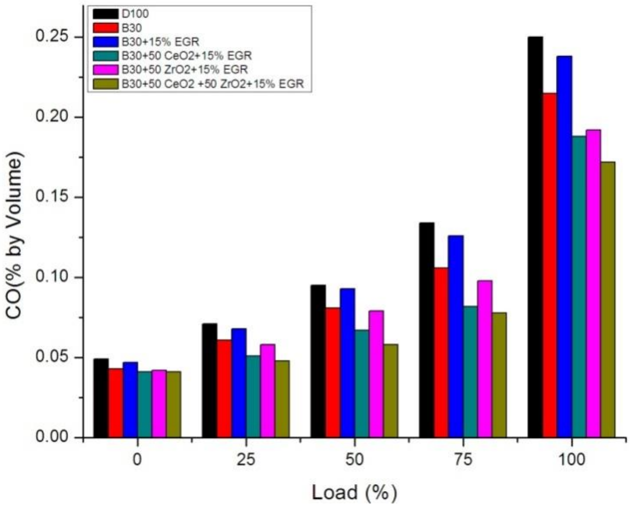

Fig. 11 Variation of CO emission with respect to load for different fuel blends

Displays the deviation of CO emission with respect to the load for different fuels at constant injection pressure at 600 bars. It is observed that biodiesel B30 blends have lower CO emission was 21% compared to diesel was 25%, due to the high intake of oxygen in biodiesel blends which leads to complete combustion. Investigations of biodiesel B30 blends with using the EGR having higher CO emission compared to B30 without EGR it caused by the unburned exhaust gas recirculation into the engine cylinder whereas lower volume of oxygen which leads to poor combustion. By adding nanoparticles in biodiesel with EGR that the sample fuel of B30+50CeO_2+15%EGR, B30+50ZrO_2+15%EGR, CO emission have been 18% and 19% respectively and the B30 with EGR was 23%. In this present research work using mixed nanoparticles with EGR B30+50CeO_2+50ZrO_2+15%EGR, CO emission results in 17% which is very lower when compared with all other fuel blends owing to the high oxygen content in nanoparticles shows in equation (3) and another reason for lower CO emission in combined nanoparticles enriched ignition characteristics which lead to shortening ignition delay period and improves better heat transfer rate, combustion flame propagation rate which provides complete combustion [6].

$$2CeO_2 + CO \longrightarrow Ce_2O_3 + CO_2 \tag{3}$$

4.2.2 HC Emissions

The formation of HC emission is extreme of poor combustion and some fuel particles do not find enough oxygen to the reaction of micro explosion and another reason for a lesser amount of oxygen available in fuel for the effect when additional fuel is accumulated in the cylinder at maximum load. The HC emissions lower at partial load, higher at full load so that unburned hydrocarbon particles released from the engine exhaust. This causes HC emission increased but hydrocarbon emission can be reduced by fuel modification. Fig. 12.

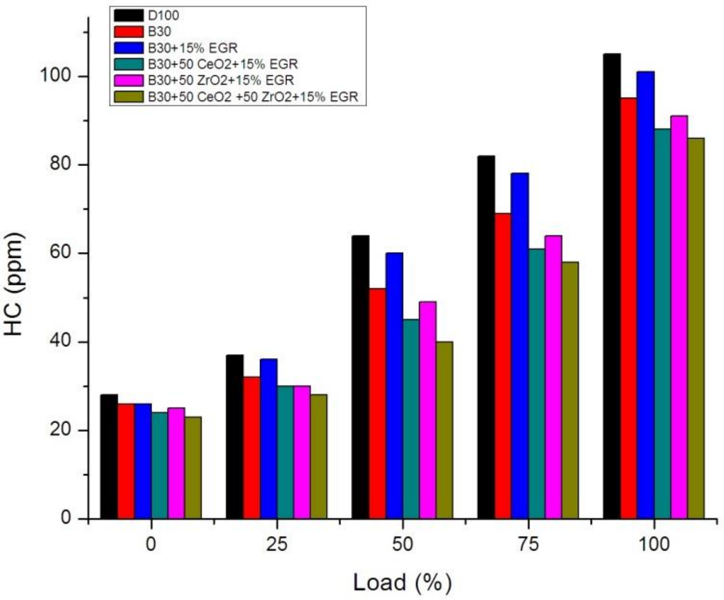

Fig. 12 Variation of HC emission with respect to load for different fuel blends

Displays the deviation of hydro carbon emission with respect to load for different fuels at constant injection pressure 600bar. It is analyzed that B30 blends have lower HC emission gave 95ppm compared to diesel was 105ppm due to high intrinsic oxygen contain in B30 blends and rising oxygen content ensuring complete combustion is liable for the decrease in HC emissions [23]. The biodiesel B30 blends are investigated in engine with and without EGR that with EGR at higher HC emissions and without EGR at lower HC emission results are 95ppm and 101ppm respectively at the same time as adding mixed nanoparticles in biodiesel with EGR, the sample fuel of B30+50CeO$_2$+50ZrO$_2$+15%EGR gives better reduction in HC emission gave 86ppm compared than B30 blends without EGR was 95ppm. Due to the nanoparticles higher surface to volume fraction and the perfect combination of a fuel with air lead to increase the oxidation during combustion.

$$(2y+x)CeO_2 + H_xC_y \longrightarrow \left[\left(2y+x\right)/2\right]Ce_2O_3 + \frac{x}{2}H_2O + \frac{y}{2}CO_2 \tag{4}$$

4.2.3 NO$_X$ Emission

Fig.13. Shows the variation of NO$_X$ emission produced in different fuel blends with respective loads. Nitrogen oxide forms with the reaction of nitrogen and oxygen gases in the presence of air during combustion at high-temperature [27]. It is spotted at constant fuel injection pressure 600 bar and full load condition in engine that the NO$_X$ utmost 1562 ppm in B30 and 1453 ppm in diesel, with coupled EGR in B30 arose exactly 1412 ppm decrease compared to diesel and B30 blends with EGR in addition to different nanoparticles CeO$_2$, ZrO$_2$ biodiesel blends have slowdown in NO$_X$ emissions consistently 1320 ppm, 1330 ppm when load increases NO$_X$ increases gradually nanoparticles starts burning at higher loads nanoparticles does not result in lower load [24]. The mixed nanoparticle blended biodiesel with EGR using the fuel sample of B30+50CeO$_2$+50ZrO$_2$+15%EGR exhibits 1192 ppm lower result compared to all the fuel blends at full load condition due to the more oxygen

presence and high flame temperature, as well as EGR, used to reduce fuel accumulation in the engine and different nanoparticle in biodiesel blends is achieve superior combustion and also proves very effectual in reducing NO_X emissions [33].

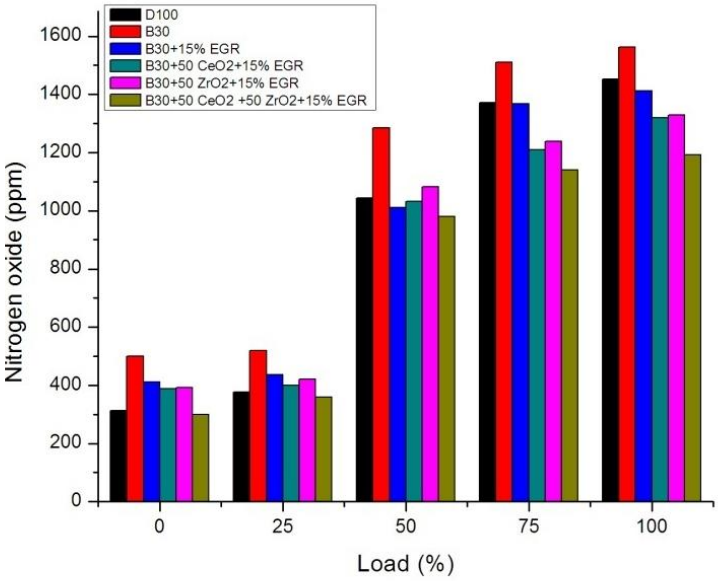

Fig. 13 Variation of NO_x emission with respect to load for different fuel blends

$$Ce_2O_3 + NO \longrightarrow 2CeO_2 + \frac{1}{2}N_2 \tag{5}$$

4.2.4 Smoke Emission

The unburned carbon spheres are generated during combustion in the combustion chamber at the maximum load where insufficient oxygen to convert all carbon atoms to CO_2 due to misfire and poor combustion . This causes soot particles and smoke emissions are increased mentioned in equation (6). The deviation of smoke emission with respect to load for different fuels are exposed in Fig. 14.

The smoke emission has different chemicals, fumes, and soot. It is investigated that the result for the biodiesel samples of B30 at full load condition there is lower in smoke 39% compared with diesel 41.5% by reason of oxygen molecules present in biodiesel so that better oxidation in the combustion process [3]. The sample fuel of B30 is investigated with and without EGR, that shows with EGR has been produced higher smoke 45.2% compared than without EGR so that caused the higher smoke for insufficient oxygen by means of exhaust gas recirculation during combustion. The other samples of mixed nano additive blended biodiesel B30+50CeO_2+50ZrO_2+15%EGR, exhibits lower smoke 37.8% compared with all other fuel blends owing to the higher surface to volume fraction and high reactivity of cerium zirconium oxide particles significantly improved in hydrocarbon oxidation, resulting in the perfect mixture of fuel with air and rapid evaporation rate in premixing phase so that can be reduced chemical delay. By this reason perfect combustion occurred in engine cylinder.

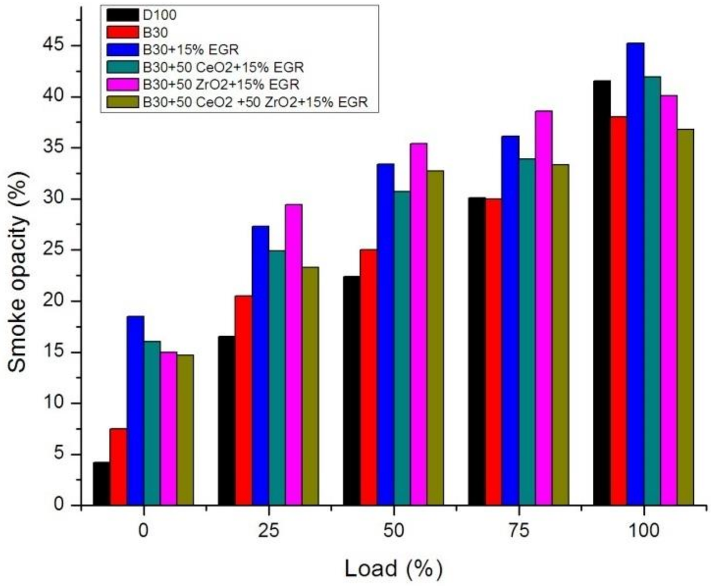

Fig. 14 Variation of Smoke emission with respect to load for different fuel blends

$$C_xH_y + zO_2 \rightarrow aCO_2 + bH_2O + cCO + dC(s) \tag{6}$$

4.3 Combustion characteristics

4.3.1 Ignition delay

Ignition delay is measured as the start of fuel injection and the start of fuel combustion into the engine cylinder. The ignition delay would be a spontaneous rise in cetane number and an inconsistent injection pressure with respect to the applicable crank angle that causes the increases peak pressure and decreases ignition delay where noticed in full load conditions while combustion in the engine [30]. Ignition delay readings measured by combustion bomb experiments and engines have been interrelated by an equation (7). Depending on the fuel ignition quality can be reducing ignition delay. There are numerous samples were implemented for the investigation that has the highest cetane number was attained 57 for Biodiesel, 47 for oil and 53 for nano additives added blended biodiesel B30 the tests were conducted through ignition delay tester as per D613 standards, like this samples have maximum heat release rate varied at start of injection and start of combustion with kept constant injection timing 23°bTDC which reduced the ignition delay, actually the finest atomization fuel where higher injection pressure stimulus ignition delay.

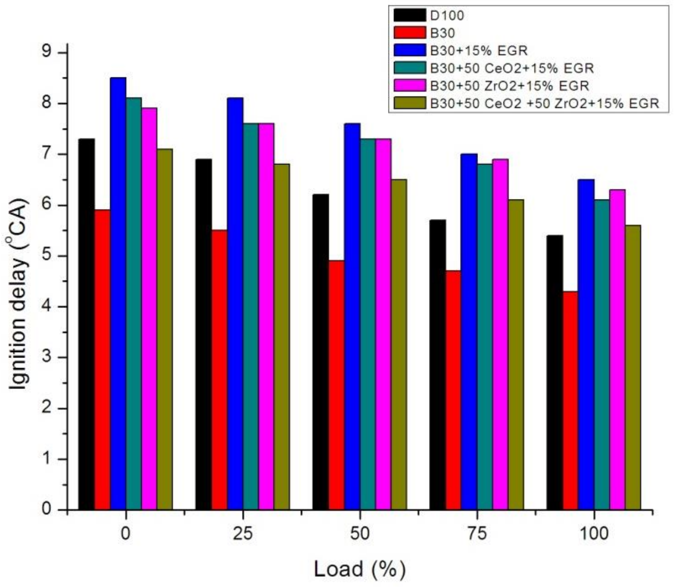

Fig. 15 Variation of Ignition delay with respect to load for different fuel blends

Fig. 15. Shows the present work has obtained values of ignition delay among samples are 4.3°CA for B30 which is lower 6.7°CA for B30+15%EGR has higher and 5.9°CA perceived for B30+CeO_2 50ppm+ZrO_2 50ppm+EGR15% thus the value nearer to the diesel D100 5.4°CA and slightly higher than B30 in high load conditions. The ignition delay problems caused by the use of EGR in biodiesel can overcome the use of Cerium zirconium oxide nanoparticle has highly reacted in the period of combustion and fuel burns very effectively.

$$\tau_{id} = AP^n \phi^m exp\left(\frac{E_A}{RT}\right) \tag{7}$$

4.3.2 Cylinder Pressure

Peak cylinder pressure is the enormity of extreme pressure which picks up due to combustion of fuel which transforms chemical energy into pressure energy; the peak pressure should impact the engine power and emissions. Fig. 16. Shows that the variation of cylinder pressure with the crank angle the cylinder pressure is an important parameter for combustion of fuel it reveals the high performance of the engine as well as heat release rate cylinder pressure raises very quickly at combustion process in the engine [15]. It is observed that cylinder pressure for different blended fuel samples worked under the full load condition at constant fuel injection pressure 600bar. In this experiment fuel, Biodiesel B30 blends increase 75.29 bar compared to Diesel 72.87 bar, Biodiesel B30 blends with EGR shows decreases cylinder pressure as 68.89 bar because of increase EGR rates causes incomplete burning of fuel. In addition to mixed nanoparticles blended fuel B30+50CeO_2+50ZrO_2+15%EGR results in 74.92 bar due to that low viscosity of fuel and nominal dosage of nanoparticles increase high oxygen whereas fine atomization enhances the high combustion [27].

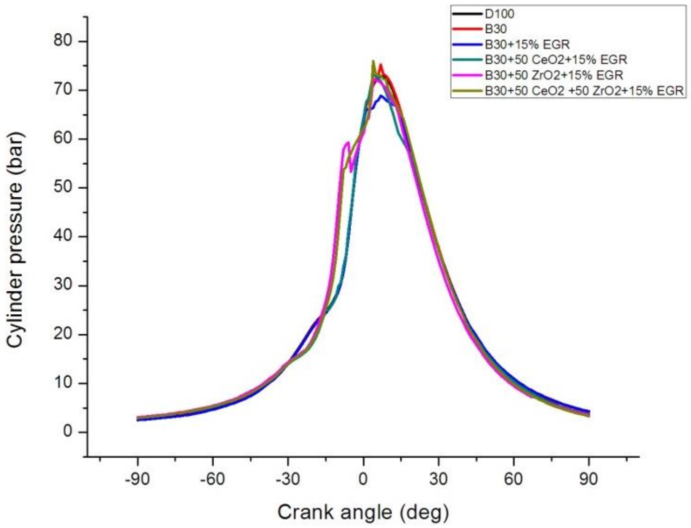

Fig. 16 Variation of Cylinder pressure with a crank angle for different fuel blends

It would roses the cylinder pressure quickly and then individual nanoparticles of CeO_2 and ZrO_2 with blended biodiesel obtained 73.18 bar and 72.23 bar.

4.3.3 The Net Heat release rate

The heat release rate measured by the first law of thermodynamics equation in (8) where $dQ_N/d\Theta$ net heat release rate, $dQ_G/d\Theta$ gross heat release rate and $dQ_{ht}/d\Theta$ heat transfer rate to the cylinder wall. Variation of Net Heat release rate with the crank angle is shown in Fig. 17.

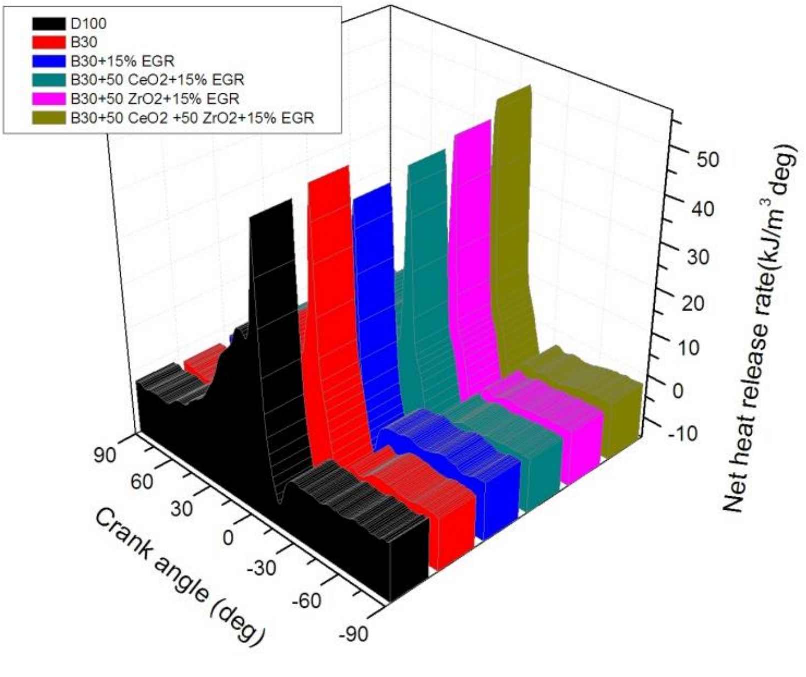

Fig. 17 Variation of Net heat release rate with a crank angle for different fuel blends

For different blended biodiesel fuel samples experienced in CRDI engine at full load condition, this is observed at constant fuel injection pressure 600bar. It is observed that the experimental value of blended fuel biodiesel B30 has 51.64kJ/m^{3}deg which is higher than

Diesel 48.88 kJ/m^{3}deg and lower heat release rate at B30 with EGR has 43.44kJ/m^{3}deg and there is no much more different in addition of individual nanoparticles of CeO_2 and ZrO_2 with EGR these were 46.69kJ/m^3 deg and 48.71 kJ/m^3 deg than that considered mixed nanoparticles of cerium zirconium blended fuel B30+50CeO_2+50ZrO_2+15% EGR has 54.98kJ/m^{3}deg it is nearer to the B30 which is better than D100 because of increasing dosage of cerium zirconium nanoparticles in biodiesel gives shorter ignition delay and improves chemical attainment reaction in fuel-air premixing phase. By this reason a higher quantity of heat released during combustion [29].

$$\frac{dQ_G}{d\theta} = \frac{dQ_N}{d\theta} + \frac{dQ_{ht}}{d\theta} \tag{8}$$

5. Conclusions

Thus the main objective of the experimental work was investigated to reduce NO_X emissions in rice bran biodiesel B30 blends as well as other emissions with an increase in engine performance. The experimental results were examined by the CRDI engine coupled with EGR. Biodiesel B30 blends with EGR resulted in decreased NO_X emission from 1562 to 1412 ppm, but other emissions were increased such as CO (21% to 23%), HC (95 to 101ppm), and smoke (39 to 45.2%). To improve this, Novel cerium and zirconium oxide mixed nano additives were blended with rice bran biodiesel. This sample (B30+50CeO_2+50ZrO_2+15%EGR) is compared with biodiesel (B30) blends and pure diesel (D100) which is mentioned below.

- NO_X emission is highly reduced from 1562 ppm to 1192 ppm.
- Other emissions such as CO, HC and smoke are also reduced from 25 to 17%, 105 to 86ppm and 41.5 to 37.8% respectively.
- Engine performance of BTE is increased from 27.09 to 31.59% and SFC is reduced from 0.34 to 0.29 kg/kWh.
- Combustion characteristics of inline cylinder pressure are increased from 72.89 to 74.92 bar and heat release rate is also increased from 48.88 to 54.98 kJ/m^3 deg and promoted complete combustion.
- Ignition delay is reduced from 6.7 to 5.9^{o}CA and which leads to better performance of the
  Combustion of the engine.

It can be concluded that the mixed nano additive blended biodiesel B30+50CeO_2+50ZrO_2+15%EGR at maximum load conditions, highly reduced NO_X emissions and simultaneously reduced other emissions compared to all fuel samples. Therefore the worth of the research which proposed the performance of optimized fuel blend and effect of the injection pressure, the nanoparticles are given significant consequence in the blended biodiesel to enrich properties and complete combustion in the engine reduced ignition delay period with increased injection pressure has acquired credits to achieve the better outcomes in the investigation thus it is finally disclosed the optimized fuel of mixed CeO_2+ZrO_2 nano additives blended biodiesel with EGR confirms enhanced engine efficiency and reduction in emission characteristics.

Compliance with ethical standards

Conflict of interest: The authors declare that they have no conflict of interest.

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