IMPACT OF CATALYTICALLY CRACKED JATROPHA OIL USING CeO₂ AND SiO₂ AS CATALYSTS ON DI DIESEL ENGINE PERFORMANCE AND EMISSION CHARACTERISTICS

by

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The biooil is thermally cracked under catalytic environment in a catalytic cracking process. This process is able to replace the transesterification process to match the biofuel properties with diesel. In this study the silicon dioxide and cerium oxide were chosen as catalyst for cracking the jatropha vegetable oil. The catalytically cracked jatropha biofuel gas is delivered at constant rate to the inlet manifold of the diesel engine. Before and after cracking, the characteristics of the catalysts were analyzed using scanning electron microscope and X-ray diffraction. The condensed cracked jatropha biofuel properties were analyzed with the results of Fourier transform infrared spectroscopy, thermogravimetric analysis, and differential scanning calorimetry analysis, and it matches with the diesel fuel. From the experimental results, the increase in brake thermal efficiency of the engine with higher oxides of nitrogen emission was observed compared with diesel for both the catalytically cracked jatropha biofuels. Notably, SiO₂ as catalyst showed the better mixing towards homogeneity with higher performance and emission results than the CeO₂ as catalyst.

Key words: Jatropha curcas, catalytic cracking, silicon dioxide, cerium oxide

Introduction

Energy is one of the basic requirements for economic development of a country. The consumption of energy has been increased day by day and becoming more dependent on depleting fossil fuels in the world [1, 2]. Rising cost of fossil fuels and related environmental issues pose greater threat to sustained economic development. Biofuels are comparatively as well as environmentally better alternative to the diesel [3-5]. Moreover, utilization of locally produced and processed fuels strengthens economy and energy security. Many researchers have experimented the usage of biofuels which are technically feasible, economical and environmental methods.

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ronmental friendly without compromising the performance of the engines [6, 7, 8]. In the conversion process of biofuel the researchers have identified that the catalytic cracking technique has given the better conversion rate [9, 10] and improves both the viscosity of fuel and calorific value of vegetable oils, and would enhance the engine performance and combustion [11, 12]. This paper compares the performance and emission characteristics of a DI Diesel engine with catalytically cracked jatropha biofuels (CCJB) and diesel. From the results the catalyst among cerium oxide (CeO₂) and silicon dioxide (SiO₂) used for cracking of biofuel will be choosen as the suitable fuel for engine application.

Materials

Catalyst

The product and rate of chemical reaction is modified by introducing a catalyst. The CeO_2 and SiO_2 are selected as catalyst for converting the jatropha oil in to a CCJB fuel. The effect of catalyst is studied through analyzing the characteristics of CCJB fuel and performance of the DI Diesel engine with CCJB gas and base diesel.

Preparation of catalyst pellets

The cerium oxide (CeO_2) and silicon dioxide (SiO_2) are commercially available in the form of powder. The catalyst is formed into pellets for the betterment of thermal cracking of biooil. The NaOH solution was used as a bonding material added with the catalyst for the preparation of catalyst slurry. The shapes of the pellets are in sphere with the approximate diameter of 20 to 30 mm, as shown in fig 1. After preparation, these pellets are kept into the oven and heated upto 80 °C for a period of one hour for solidification.



Figure 1. Pellets of catalyst; (A) CeO₂, (B) SiO₂

The pellets are placed in the reactor and then exposed to a constant heat of 250-300 °C temperature. The jatropha oil freely flows in to the reactor at constant rate, where it is cracked and converted into gaseous form. Finally, cracked jatropha oil in the gaseous state is directly sent to engine intake manifold.

Characterization of catalysts

The catalysts are characterized with the help of scanning electron microscope (SEM) and X-ray diffraction (XRD) for analyzing its aptness. In fig. 2, A-I and A-II show the SEM images of CeO_2 catalyst for before and after cracking.

The state before cracking of CeO_2 catalys indicates clearly the irregular morphologies with high porous structure having the particle size from 5 to 25 μ m. This structure will be

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more useful for allowing biooil to penetrate for higher rate of chemical reactions and reduces the weight of the catalyst chamber. In fig. 2, A-II confirms the expected structural change, that was visible as color change after cracking.



Figure 2. The SEM images of CeO₂ catalyst before (A-I) and after (A-II) cracking

The XRD results clearly show that there was no change in the components before and after cracking in fig 3. The additional components such as Cu and Na present in the after cracking may from impurities in the surroundings, because the reaction is happening open environment. Second part of this study, the same procedure is followed for SiO_2 as catalyst. In fig. 4, B-I and B-II show the SiO_2 catalyst before and after catalytic cracking.



Figure 3. The XRD images of CeO₂ catalyst before (A-I) and after (A-II) cracking

The SEM images of SiO_2 have regular and irregular in shape and the particle sizes vary from 2 to 20 μ m. The reactions were pretty similar to the case of CeO₂. The XRD result also confirms the same in the fig 5. The presence of Na indicated in fig 5. B-II represents the bonding material added during pellet preparation [13].

Jatropha vegetable oil

The jatropha vegetable oil is widely used by the researchers as an alternative fuel due to its favorable properties and availability. Many researchers have tried out with trans-



Figure 4. The SEM images of SiO₂ catalyst before (B-I) and after (B-II) cracking



Figure 5. The XRD images of SiO₂ catalyst before (B-I) and after (B-II) cracking

esterification process for conversion of biooil and used in engine at various proportions with diesel. The results showed its potential to be used as an alternative fuel. The physical properties of jatropha oil, SiO_2 , and CeO_2 CCJB oils and diesel are shown in tab. 1. The calorific value of CCJB is higher may be because of the presence of more alkanes and oxygen in the fuel [10, 13].

Properties	Diesel	Jatropha curcas oil	CCJB by CeO ₂	CCJB by SiO ₂
Density [gcm ⁻³], 30 °C	0.836-0.85	0.933	0.87	0.854
Kinematic viscosity [cSt]	4-8	52.76	12.1	11.7
Flash point [°C]	45-60	210.00	51	52
Calorific value [MJkg ⁻¹]	42-46	38.20	40.5	40.2

Characterization of cracked jatropha oil

The cracked fuel from catalytic reactor is in the gaseous form. The gaseous CCJB is condensed and the oil is used for finding its physical properties. The condensed fuel is further

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characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and differential scanning calorimetry analysis (DSC).

The infrared spectroscopy absorptions for the CeO₂ and SiO₂ CCJB fuel, shown in figs. 6 and 7, lies between 3000-2800 cm⁻¹ frequency regions. It confirms that the cracked jatropha oil samples have alkane family with single carbon-carbon bonds. The peak lies at around 1700 cm⁻¹ frequency region confirms the C=O bond present in the CCJB. These results are nearly similar to the diesel fuel.



Figure 6. The FTIR image of CCJB by CeO₂ catalyst

Figure 7. The FTIR image of CCJB by SiO₂ catalyst

The thermal behavior of the fuel studied using TGA and DSC analysis are shown in figs. 8. and 9, for the CeO₂ and SiO₂, respectively. The CeO₂ sample has two peaks at 356.5 and 414.4 °C, where at 356.5 °C, there is an endothermic reaction for an area of 7.895 J/kg. The SiO₂ sample is also having two peaks at 272 and 438 °C. This gives an outlook of the quality of mixing for high homogeneity. The higher percentage in change of mass for a small change in temperature for the SiO₂ sample implies the quality of mixing and homogeneity [14].



Figure 8. The TG and DSC of CCJB by CeO₂ catalyst





Figure 9. The TG and DSC of CCJB by SiO_2 catalyst



Figure 10. Flowchart of methodology

Methodology

The procedure followed for analyzing the performance of the selected catalyst in catalytic cracking process is given in fig 10. The catalyst is analyzed in two phases wherein, the first phase discussed the characterisation of catalyst CeO₂ before and after cracking, and the performance of the engine with the CCJB fuel and the second one with the SiO₂ as catalyst. Finaly, the performance of the engine with CCJB fuel is compared with the base diesel performance.

Experimental set-up

The engine used for this study is a stationary single cylinder constant speed (1500 rpm), four stroke and DI Diesel engine. The engine is coupled with an eddy current dynamometer. The detailed specification of the engine is listed in tab. 2. The arrangement of engine set-up with fuel reactor in the engine intake manifold is shown in fig. 11. The CCJB B20 fuel is used for different load conditions, derived from the specific fuel consumption of diesel.

The uncertainty analysis was performed based on the list of measurement uncertainties of various equipment's used in this study are shown in tab. 3 and the total uncertainty was found to be $\pm 2.79\%$ [1].

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Table 2. Test engine specification

Description	Particulars	Description	Particulars
Make	Kirloskar-TV 1	Rated output	5.2 kW
Bore	87.5 mm	Injection pressure	220 bar
Stroke	110 mm	Fuel injection timing	23 CA bTDC
Compression ratio	17.5:1	Lubricating oil	SAE 40

Table 3.	Accuracy	and	uncertainty	y of the	e instruments
	•/			/	

Measurement	Instrument	Accuracy	Uncertainty [%]
Fuel consumption	Burette	$\pm 0.2 \text{ cm}^3$	1.5
Loading device	Load cell	±10 N	0.2
Speed	Speed sensor	$\pm 10 \text{ rpm}$	1.0
Temperature	Temperature indicator	±2 °C	0.3
СО		±0.02%	0.2
НС	Exhaust gas analyzer	$\pm 10 \text{ ppm}$	0.1
NO _x		±12 ppm	0.2
Smoke density	Smoke meter	$\pm 1 \text{ HSU}$	1
Cylinder pressure	Pressure transducer	±0.3 kg	0.3
Crank angle	Crank angle encoder	±1°	1

Results and discussion

Performance characteristics

The effect of catalyst in cracking of biofuel was analyzed in terms of engine performance. The fuel which gives higher brake thermal efficiency (BTE) with lower specific fuel consumption has to be chosen for engine application. In this study two catalytically cracked biooils have taken and they give higher BTE than base diesel (fig 12). This is due to the gaseous induction of catalytically cracked fuel and it enhances the premixed combustion. The SiO₂ CCJB has given the highest BTE due to the higher mass change at 200 to 300 °C which leads to more gaseous phase in which cracking



Figure 11. Schematic diagram of the engine experimental set-up

is happening. The BTE is same for both the CCJB oils at lower load and it is high for SiO₂ cracked CCJB at higher loads. This may due to the shorter duration of combustion than CeO₂ catalyst. The BTE is higher for the SiO₂ at an average of 17.49 and 13.32% higher for CeO₂ catalyst at different load conditions when compared with that of diesel fuel. The average increase in BTE for SiO₂ than CeO₂ is around 4.7%.





Figure 12. Variation of BTE with brake power

Figure 13. Variation of SFC with brake power

The specific fuel consumption (SFC) is showing similar trend of BTE in fig 13. The change in BSFC is 7 and 5% for the SiO_2 and CeO_2 catalyst. This clearly indicates the importance of premixed combustion phase of a diesel engine.

Combustion characteristics

The combustion characteristics were analyzed for different fuels at different loading conditions. The in-cylinder pressure indicates the work output available at the crank from the piston. The rate of pressure rise will give the insight of rate of fuel burning. The premixed combustion phase is more in the case of CCJB fuels could be visualized in higher heat release rate and BTE. The delayed and bulky combustion was observed and evidenced in higher NO_x emission. The higher after burning phase of CeO₂ has been seen and shown with the lower HC emission. The combustion duration is less in the case of CCJB than diesel and in particular with SiO₂ CCJB fuel.

The variation of heat release rate with respect to crank angle for the substituted CCJB by SiO₂ and CeO₂ catalyst along with diesel at different load conditions has been portrayed in fig. 14. The higher heat release rate is observed for the CCJB fuels due to complete mixing and air and fuel. The early start of combustion as well as more after burning phase is seen for the CeO₂ catalyst than the diesel and SiO₂ catalyst fuel. The SiO₂ catalyst has shown the peak heat release rate than other envisaging from the *P*- θ diagram shown in fig. 15.



Figure 14. Variation of heat release rate with crank angle

Figure 15. The *P*-θ diagram

Emission characteristics

The stringent emission norms have to be considered while selecting a fuel. The regulated emissions are considered for analysis. The smoke is an additional emission of diesel engine and it indicates the level of diffusive combustion. The premixed combustion phase reduces the chances of producing smoke emissions. The biooil contains the oxygen in it will tend to increase in premixed combustion but still the property like viscosity and the sauter mean diameter of the injected fuel will affect the smoke formation. Less smoke was observed in this study for the substituted CCJB fuels due to its gaseous nature when compared to diesel (fig. 16).

The biofuels have the tendency of producing more NO_x emission than diesel due to it bulky combustion due to its viscosity and the oxygen content in the fuel. The higher premixed combustion phase will increase the in-cylinder temperature which in turn enhance the viability of NO_x formation. In this study, the premixed combustion due to hot gaseous induction shows the higher NO_x levels for CCJB fuels. The SiO₂ catalyst has given the higher NO_x emission than other fuels which can be seen from its higher BTE and heat release rate. The NO_x emission is increasing with the increase in load for CCJB fuels. The maximum variation of NO_x emission formed is of 27% and 33% higher than diesel for SiO₂ and CeO₂ catalyst shown in fig. 17.



Figure 16. Variation of smoke density with brakepower

Figure 17. Variation of NO_x with brakepower

The HC emission will give the quality of oxidation during combustion. The higher value of HC emission is observed in the case of SiO₂ catalyst when compared with diesel and CeO₂ catalyst. The reaction is due to its higher homogeneity in mixing (fig. 18). The mass change at lower temperature range observed in TGA and DSC curves have given more insight to this homogeneous phenomenon in SiO₂ catalyst. The CeO₂ catalyst has given the lesser HC emission which is due to the early start of combustion and combustion duration seen from the heat release rate curve. The CO emissions for the CCJB fuels are lesser than diesel and shown in fig. 19. The oxygen content in the supplement fuel will increase the oxidation reaction during combustion which tends to reduce the CO emission. Among the CCJB fuels, the SiO₂ CCJB has shown higher CO due to higher homogeneous mixing due to its mass change at 200 to 300 °C.



140 HC [ppm] 120 100 80 60 Diesel 40 SIO 20 CeO, 0 ò 20 80 40 60 100 Brake power [%]

Figure 18. Variation of HC with brake power

Figure 19. Variation of CO with brake power

Conclusions

The following conclusions are drawn based on the experimental investigations.

- The SiO₂ CCJB has some favorable results when compared with CeO₂.
- High peak heat release rate for CCJB fuel. The higher homogeneity mixing of fuel and air leads to higher peak heat release rate with the SiO₂ catalyst.
- The more premixed combustion phase helps in getting the higher peak pressure than the diesel for CCJB fuels. The lesser combustion durations also achieved for CCJB fuels. So the BTE is increasing with the CCJB fuels than diesel.
- The considerable decrease in smoke emission was obtained for the CCJB fuels. In this connection, much higher pronounced premixed combustion phase for cracked jatropha gas substantiates the reasons for increased NO_x emission. The HC emission is higher with SiO₂ as catalyst may due to the homogeneity.
- The CO emissions shows noticeable difference in all loads other than 20% load. The reason for getting lesser CO emission is because of the presence of oxygen content and higher in-cylinder temperature.
- By observing the results the SiO_2 fuel has given the better results than the other fuels. The homogeneity was obtained while utilizing this fuel can be seen through high BTE, incylinder pressure and peak heat release rate along with high HC and CO emissions. The NO_x is higher than diesel but lesser than CeO₂ is also an indication of better mixing.

From these results, among the selected SiO_2 and CeO_2 , as a catalyst for cracking a biooil, the SiO_2 as the better choice.

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