

Preparation of Bio-Fuel by Catalytic Cracking of Mahua Oil and Its Impact on a Diesel Engine Performance

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ABSTRACT

In this paper, the process parameter evaluation and catalyst performance studies were conducted to produce biofuel from *Mahua* oil and coal fly ash (CFA) selected as a catalyst and biofuel was produced in the fixed bed catalytic cracking reactor at temperatures ranging from 400 °C to 450 °C under atmospheric pressure. The properties of produced biofuels were compared with the ASTM D6751 standards. The resulting biofuels were characterized by FTIR (Fourier-transform infrared spectrometer) and GC-MS (Gas chromatography-Mass spectrometer). The performance of engine emission and combustion parameters were investigated with various blends. The peak cylinder pressure and the heat release rate (HRRs) for B25 *Mahua* blends are slightly higher than other blends. Decreased in NO_x emission for B100 with increasing the concentration of the *Mahua* blends but on the other hand the CO and HC emission were slightly increased with all load.

Keywords: Biodiesel, Catalytic Cracking, Mahua oil, Coal Fly Ash and Emissions

1. INTRODUCTION

Energy is a fundamental commodity that is required by any industrialized nation. It is now known that the global fossil fuel reserves are shrinking and forecasted to be depleted in the near future while the world energy demand increases every year. Concurrently, the staggering evidences of global warming are mandating the reduction of greenhouse gas emission into the atmosphere. These two facts combined have provided a strong motivation for the search and development of environmentally friendly alternative fuels that can be guarantee continued energy supply. Since its birth, vegetable oil was always considered as a suitable fuel for the diesel engine [1].

Biodiesel is a green fuel considered a potential substitute of conventional diesel. It has been proved to be biodegradable, renew-able and offer reduced emissions of CO₂, SO₂ particulates and hydrocarbons compared to fossil diesel [2]. Among the many possible resources, biodiesel got the much attention as a promising substitute for conventional petrol-diesel fuel. It is defined as fatty acids methyl esters (FAME) obtained by the transesterification of vegetable oils or animal fats with alcohols [3]. During transesterification, the glycerin that is formed needs to be removed so that it is not converted into formaldehyde or acetaldehyde when burned because both would pose a health hazard [4]. Basecatalyzed transesterification is much faster than acid-catalyzed transesterification and is the most commonly used method commercially [5].

Unlike many of the recently suggested alternative liquid biofuels, the fundamental chemistry of vegetable oil transesterification or esterification has been well studied and several production facilities are operational. It is in this environment that biodiesel has emerged as a promising renewable liquid fuel and the most likely replacement for

petrol diesel. Biodiesel is produced through transesterification process, but it has some disadvantages such as low ignition point, incomplete combustion, and it should blend with fossil fuels for utilization. Currently, homogeneous base catalysis (NaOH or KOH) is preferred for the conversion of edible refined vegetable oil to biodiesel. The production of biodiesel from the transesterification process has lots of problem and disadvantages which include highly unsaturated content (corrosion problems), poor storage stability, unfavorable for cold conditions, low energy content, and methane content is toxic, and higher cost compared to conventional fuel. To overcome these problems and to attain better quality, the alternative chemical conversion of triglyceride-based feeds, mainly hydrocarbon rich in paraffin's, are under intensive research worldwide. While this approach has many merits, but unfortunately results in a final product more expensive than conventional diesel primarily because of the high cost of the feedstock and the extensive separation steps required to achieve fuel grade specifications [6]. New catalytic routes are consequently under investigation to improve the competitiveness of biodiesel.

Dessy Y. et al. [7] conducted experiments on catalytic cracking of palm oil to produce biodiesel. From the result it was found that MCM-41 is promising catalyst for biofuel production from palm oil. The maximum organic liquid product is 60.73 % was obtained at the O/C ratio of 32.50 and WHSV of 19.38/hour. The use of the solid base catalysts possesses potential for new developments in the production of biodiesel; allowing process simplification and offering reduction in processing costs by improving the mass transfer limitation of the three phase reaction and simplifying the product purification processes compared to what is required in conventional homogeneous catalysis [8].

Coal fly ash (FA) is an inorganic residue and a waste product arising from the coal combustion processes in coal-fired power stations. The global annual production of FA is about

800 million tons and this amount has been predicted to increase in the future [9]. Catalytic cracking process is used to produce bio fuel rich in different fractions (gasoline, diesel and kerosene) from edible and non-edible oils [10]. Zerihun Demrew et al [11]. In their research, catalytic cracking of vegetable oil using metal oxides (Co₃O₄, KOH, MoO₃, NiO, V₂O₅, and ZnO) as catalysts. The maximum conversion observed was 87.6%, and the physical properties of the product obtained were in agreement with the standard values. Methyl and ethyl esters were found to be present majorly in the product obtained. Biodiesel usually includes a small percentage of diglycerides having higher boiling points than diesel. However, the chemical reactions during the injection of biodiesel at high temperature resulted in the breakdown of the high-molecular weighted esters. These complex chemical reactions led to the formation of gases of low-molecular weight. Rapid gasification of this lighter oil in the fringe of the spray spreads out the jet, and thus volatile combustion compounds ignited earlier and reduced the delay period. Biodiesel derived from jatropha, karanja and polanga oil having higher molecular weight is likely to react identically [12]. When the engine is running in idle conditions, it takes a rich mixture of air and fuel, such that the fuel consumption rate is high. Furthermore, during idling, the engine is not able to work at peak operating temperature and the combustion of fuel is incomplete, which leaves fuel residues in the exhaust and thus, emission levels increases. As biodiesels application in diesel engine will increase day by day, more studies needs be conducted to find out the impact of using biodiesel on fuel consumption and exhaust emissions of diesel vehicles at high idling condition [13]. The catalyst showed good stability during the recycling experiments and it was sustained for four consecutive runs. K-zeolite synthesized from coal fly ash is cost effective catalyst for glycerol carbonate synthesis via transesterification of glycerol with DMC and it offers a novel opportunity to utilize waste coal fly ash [14].

Hence, the catalytic cracking of vegetable oil has been chosen in the present investigation with the focus to produce biodiesel. The way of producing biodiesel is by catalytic cracking of oil at lower temperatures (450-500°C) which gives highly selective hydrocarbon [15]. The cost of biodiesel can be reduced by choosing less expensive feedstock such as non-edible oil, waste cooking oil, and animal fat and also by selecting a less expensive catalyst. *Mahua oil* is one such kind of oil which is non-edible, has high free fatty acid content and is toxic in nature. It is easily available and it can grow well in the Indian climate and also even in degraded lands where water is scarce. Fly ash, the chief inorganic waste, arises through coal combustion processes at coal-based thermal power plant; the presence of high amount of SiO₂ and Al₂O₃ prompts its potential applicability as a low-cost catalyst support [16].

2. MATERIALS AND METHODS

2.1. Mahua oil (Madhucaindica)

Raw *Mahua* oil were collected from the local market. This is one kind of tropical tree found in northern and central plains and forests. This is most probably called as illupai or mahua (Madhucaindica). This *Mahua* tree grows to the level of 60-70 feet height and this mahua belongs to the sapotaceae family.

This is more prominently seen in Jharkhand, Uttar Pradesh, Bihar, Maharashtra, Madhya Pradesh, Kerala, Gujarat and Orissa. The table 1. Shows the composition of free fatty acid present in the raw *Mahua* oil.

Table 1. Composition of raw mahua oil (17)

Sl.No.	Properties	Weights (%)
1.	Arachidic	2.1
2.	Linoleic	12.5
3.	Oleic	41.1
4.	Palmitic	23.0

2.2. Coal fly ash (CFA)

Coal fly ash generally collected from the Mettur thermal power plant, Salem, Tamilnadu. Fly ashes is generally defined as a “fine-grained powder, highly heterogeneous, low-cost catalyst support and consisting of a mixture of glassy particles with various identifiable crystalline phases such as quartz, mullite, and various iron oxides [18]. The combustion of pulverized coal produces two main solid byproducts: bottom ash, and fly ash. Bottom ash remains at the bottom of the furnace, Fly ash, which forms between 60 and 88 wt% [19] of the solid residue is considered a pollutant if unused, and requires disposal. The main source of fly ash is from coal burning thermoelectric power plants. Raw (untreated) coal fly ash consists of predominantly silica (SiO₂), alumina (Al₂O₃) and iron oxides (Fe₂O₃). The most common elements (>1%) are oxygen, silicon, aluminium, iron, calcium, magnesium, sodium, potassium, sulphur and carbon.

2.3. Catalytic cracking process

The catalytic cracking reaction of vegetable oils has been carried out in catalytic cracking reactor made of iron material. The reactor is heated by electrical coil and the temperature of the reactor is measured by a thermocouple, provided gas delivery system and provision for sampling. An on/off temperature controller was used for controlling the temperature. Catalytic cracking experiment were conducted at the optimum temperature, at different ratios of catalyst were analyzed to identify the yield of biofuel production. In this experimental section the catalyst used directly without any treatment Add coal fly ash with *Mahua* oil and make it as a slurry with help of stirrer and Fed into the catalytic reactor and it is heated up to 450-500 °C . On heating, due to catalyst activity the catalytic cracking reaction takes place. The gaseous hydrocarbon will release from vegetable oil, come through the condenser, gets cooled and collected in the form of liquid hydrocarbon and table 3. Shows the properties of cracked biofuels were analyzed in ETA lab, Chennai, India.

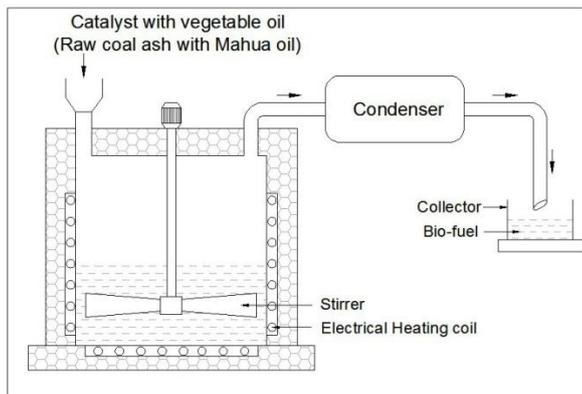


Fig 1. Catalytic cracking reactor

The GC (gas-chromatograph) was applied for the evaluation of *Mahua*biofuel derived from catalytic cracking process. The bio fuels was characterized with a 5975Cgas chromatograph with a 30m×0.25mm×0.25um DB-5ms Agilent ID capillary column coated with polysiloxane and the GC parameters were as follows.

The temperature for the oven operated in this program start at 70°C for 3 min and increased at a rate of 9°C/min to 300°C and helium 99.9995% purity as the carrier gas with a flow rate of 1.5 ml/min. The *Mahua*oil chromatogram were collected with their retention time and characterized using the GC-MS spectrometer to know the content of compounds in the biodiesel, shown in Fig. 2, and each compound shows separate peaks which are shown in Table. 2andidentified the formation of olefins, paraffins and carboxylic acids in the cracked biofuels during their analyses.

2.4. GC analysis

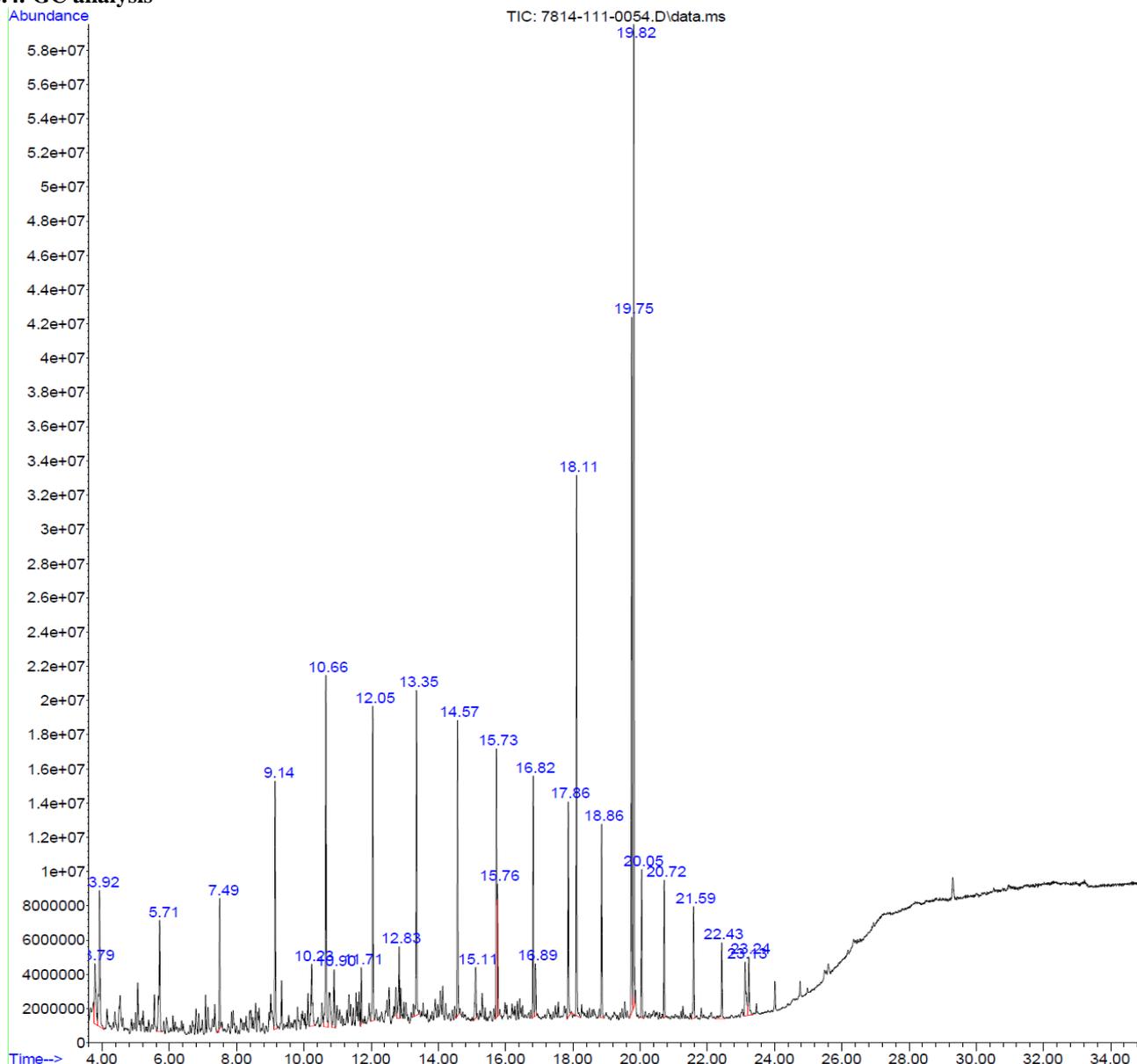


Fig 2. GC analysis for catalytic cracking biofuel

Table 2. Chemical characterization of Mahuaoil by catalytic cracking process

Peak No.	Time	Component	Peak No.	Time	Component
1	3.918	Nonane	12	18.105	Hexadecanoic acid, methyl ester
2	5.705	Decane	13	18.855	Eicosane, Heptadecane
3	7.493	Undecane	14	19.752	9,12-Octadecadienoic acid (Z,Z), methyl ester
4	9.141	Dodecane	15	19.810	9-Octadecenoic acid, methyl ester
5	10.655	Tridecane, Tetradecane	16	20.045	Methyl stearate
6	12.048	Tetradecane	17	20.720	Nonadecane, 9-methyl
7	13.346	Pentadecane	18	21.591	Hexacosane, Tricosane
8	14.567	Hexadecane	19	22.431	Tetracosane
9	15.725	Dodecane,2,6,11-trimethyl	20	23.124	Phenol, 3-methyl
10	16.820	Octadecane	21	29.302	Cyclopenta[5,6]naphth[2,1-c]azepin-3(2H)-one, 8.beta.-(1,5-dimethylhexyl)
11	17.863	Nonadecane			

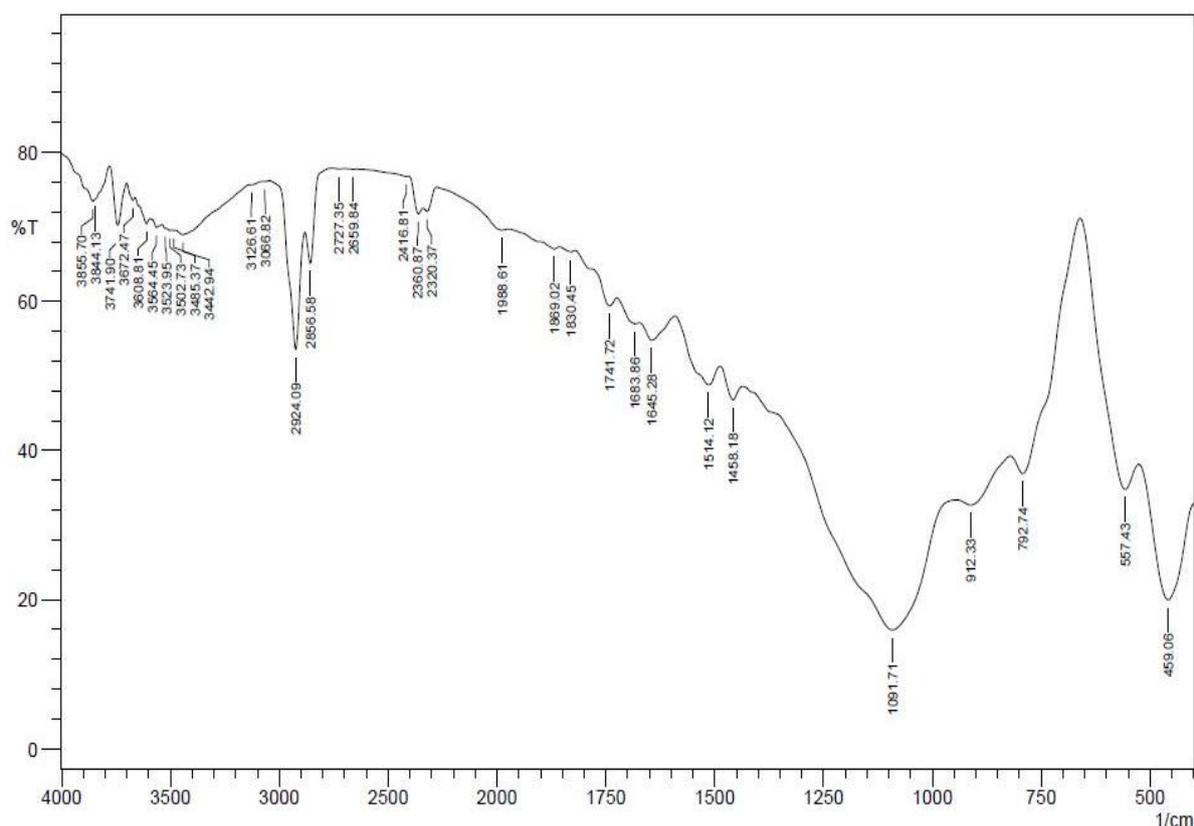


Fig.3 FTIR spectroscopy of CFA used mahua oil

2.5. FTIR spectrum analysis

FTIR spectroscopy was used to referring in correlation by groups are Identified. FTIR spectrometry had done by order the overcome the limitations with dispersive instrument. The main difficultly is the slow scanning process. The FITR spectra representing the functional group compositional analysis of CFA using *Mahua*oil FITR spectra were recorded using (Instruments Name and place). The spectra's of CFA the shows absorbance bands characteristic cracked fly ash of 2922.16 CM^{-1} and 2852.72 CM^{-1} and related to C-O and C=O stretches, respectively. Also it shows C-H stretches in

RFA 2924 CM^{-1} and 2856 CM^{-1} . The spectrum cracked fly ash 1423 CM^{-1} area indicated C=O groups of phenolic compounds. The C=C bands in aromatic and branch rings, so that the absorption stay. From the FTIR spectrum of CFA using *Mahua* oil had absorption bands in the region 4000-400 CM^{-1} . The peak of absorption off groups indicated that phenolic compounds appeared at a frequency 3120.82 CM^{-1} Figure 3. Shows the CFA using the IR spectra, it's indicated that the cracked fly ash consist of saturated hydrocarbon. The

presence of hydrocarbon groups. C-H indicates that the liquid has a potential to be used as fuels.

Table 3. Properties of diesel fuel and cracked Mahuabiofuel

Properties	Measurement standards	Diesel	Cracked biofuel
Specific gravity @ 15/15cc	ASTM D 445	0.8234	0.8568
Kinematic viscosity @ 40 c in Cst	ASTM D 445	3.06	6.10
Flash point	ASTM D 93	33C	37C
Fire point	ASTM D 1160	37C	41C
Grass calorific value kcal/kg	ASTM D 240	10.132	10.008
Calculated cetane index	ASTM D 976	52	43
Density @ 16 C lin gm/cc	ASTM D 1298	0.8225	0.8560

3. EXPERIMENTAL SETUP AND ARRANGEMENT

The test engine used in the current study is a stationary single cylinder diesel engine, used mainly for agricultural application and in industries for generating electricity. The engine is coupled with an eddy current dynamometer for applying loads by adjusting the Current Supplied to it and while doing this; the fuel pump rack position is adjusted so as to maintain a constant speed of 1500 rpm. All other engine specifications are listed in table 4 and the arrangement of engine setup has been depicted in a schematic diagram as shown in figure 4. The fuel flow rate was measured manually using a burette and stopwatch, and airflow rate was measured using an orifice meter, installed in the intake air supply system. Measurement of combustion chamber pressure was obtained by installing an AVL pressure transducer with the sensitivity of 16:11 pC/bar. The in-cylinder pressure was recorded 207 for 100 cycles using AVL 619 Indimeter hardware and Indwin software version 2.2, and the recorded pressure signals are then processed to estimate the heat release rate. Exhaust emissions such as HC (Hydrocarbon), CO, NOX (oxides of nitrogen), and O2 (oxygen) were measured using an AVL-444 di-gas analyzer, which works on NDIR (non-dispersive infrared) principle by selective absorption. The exhaust sample to be evaluated was passed through a cold trap (moisture separator) and filter element to prevent water vapor and particulates entering into the analyzer. Notably, the gaseous emissions such as HC and NOX were measured in ppm (parts per million), while CO and O2 emissions were measured in terms of percentage volume. Smoke level in the exhaust was measured in terms of HSU (hartridge smoke unit) using a standard AVL437C smoke meter based on light extinction principle. Suitable blend of cracked Mahuaoil with diesel such as B25 (25% cracked Mahuaoil and 75% diesel), B50 (50% cracked Mahuaoil and 50% diesel), B75 (75% cracked Mahuaoil and 25% diesel) and B100 (100% cracked Mahuaoil) were prepared for testing in diesel engine. Once the engine is set to operate, it is fueled by the test fuels and all these testing have been carried out at ambient conditions.

Table 4. Specifications of the test engine

Type	Vertical, Water cooled, Four
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	stroke
Number of cylinder	One
Bore	87.5 mm
Stroke	110 mm
Compression ratio	17.5:1
Maximum power	5.2 kW
Speed	1500 rev/min
Dynamometer	Eddy current
Injection timing	23° before TDC
Injection pressure	220 kgf/cm ²

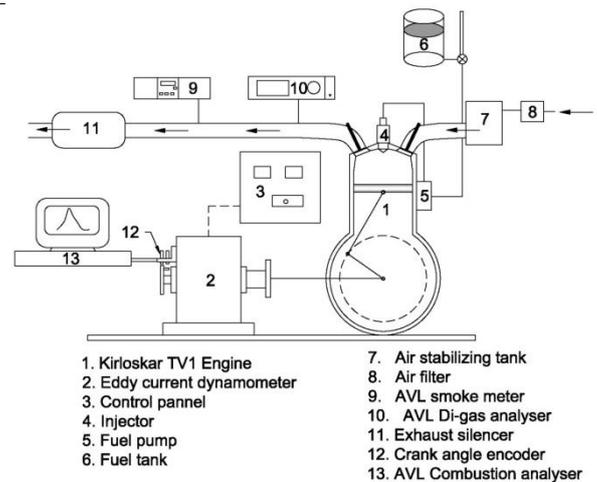


Fig 4. Experimental setup (Kirloskar TV-I Engine)

4. RESULTS AND DISCUSSION

4.1. Brake thermal efficiency

The variations of BTE with load for different blends are shown in Fig 5. In all cases the brake thermal efficiency has the tendency to increase with increase in applied load. This is due to the reduction in heat loss and increase in power developed with increase in load. The thermal efficiency of all blends of Mahuabiodiesel lower than that of neat diesel. This is due to poor mixture formation as a result of low volatility, higher viscosity and higher density of biodiesel. The thermal efficiency of B25 blends gives the higher efficiency compared to other blends namely B50, B75 and B100. The possible reasons for this reduction are lower calorific value and hence increase in fuel consumption as compared to diesel fuel. Bhupendraet al. [20]

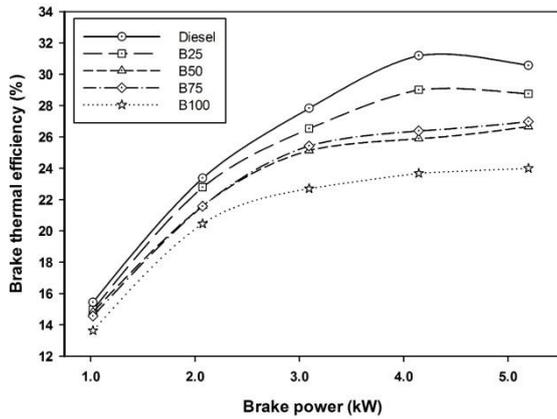


Fig 5. Variations of break thermal efficiency Vs brake power

4.2. Smoke density

The variation of smoke density with respect to load is shown in Fig 6. It is observed that smoke reducing effect could be attributed to its displacement of aromatic and short-chain paraffin hydrocarbons. It is observed that all biodiesel blends were lowered compared to diesel in low smoke opacity because of high amount of oxygen present in the biodiesel blends which tend to reduce the smoke opacity this is due to lower carbon molecule and higher oxygen content can decrease the tendency of a fuel for soot production and reduce the smoke opacity. From GC-MS (Table 6), the presence of octadecane (C₁₈H₃₈) in the biodiesel that leads to improve the significant reduction of smoke opacity [21, 22].

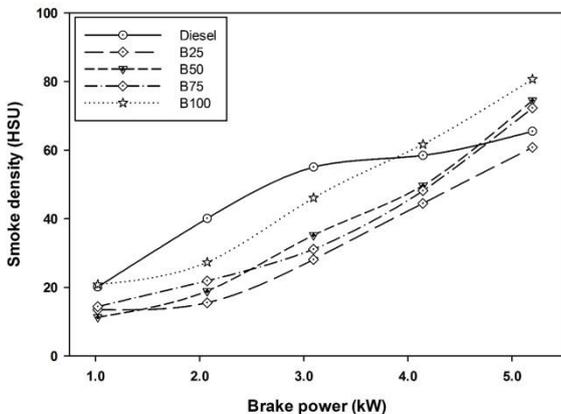


Fig 6. Variations of smoke density Vs brake power

4.3. Oxides of nitrogen

The variation of oxides of nitrogen with respect to the load is shown in Fig.7 indicates that blends of biodiesel exhibited lowest NO_x emission at all load conditions compared to neat diesel fuel. This is due to poor atomization of biodiesel blends and lower cetane number which leads to poor combustion and resulting lower NO_x emission puhan et al[23]., In case of B100, NO_x emission is lower than other blends. NO_x concentration increased with the increase in load of biodiesel blends, however, the NO_x emission of diesel higher than biodiesel blends attains maximum at 5.2kW for all the blends. In case of diesel, B25, B50, B75 and B100, NO_x, the rates of emission recorded were 1126, 654, 635, 645 and 636 ppm respectively.

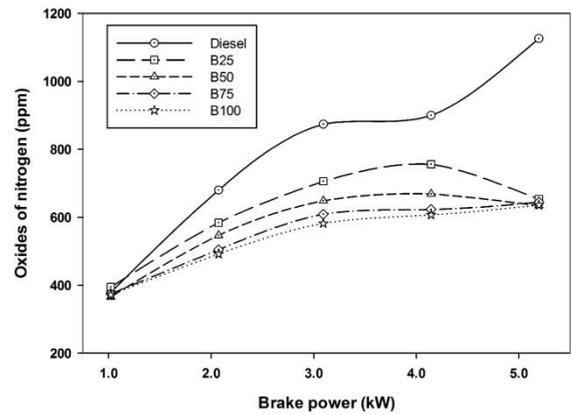


Fig 7. Variations of oxides of nitrogen Vs brake power

4.4. Carbon monoxide

Variation of CO emission with respect to engine loads for different fuel blends is shown in fig 8. It is observed that CO emission of all biodiesel blends at initial conditions, decreased and increased with full load. B25 exhibits the lowest emission then other blends, however diesel produce the lowest emission then biodiesel blends due to incomplete combustion of fuel and it is produced most readily from petroleum fuels, which contain no oxygen in their molecular structure. MetenGumus et al[24]., Generally, CO emissions is affected by the air-fuel equivalence ratio, fuel type, combustion chamber design, atomization rate, start of injection timing, injection pressure, engine load and speed.

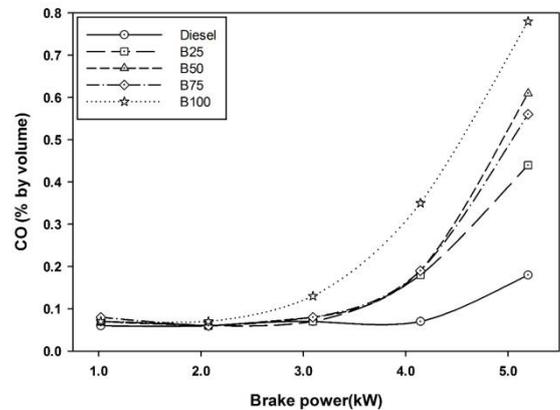


Fig 8. Variations of carbon monoxide Vs brake power

4.5. Hydrocarbon

The variation of hydrocarbon with respect to load is shown in fig. 9. UHC emission consist of fuel that is completely unburned or only partially burned. UHC emissions result from the problems of fuel and air-mixing, and largely unaffected by the overall air-fuel equivalence ratio. The unburned hydrocarbon emission of blends of biodiesel is more when compared to that for neat diesel for all loads. This is mainly poor mixture formation tendency of blends of biodiesel. In addition to the other factors, the lower thermal efficiency with these blends also is responsible for this trend. It may be noted that a lower thermal efficiency with these blends will lead to injection of higher quantities for the same load condition.

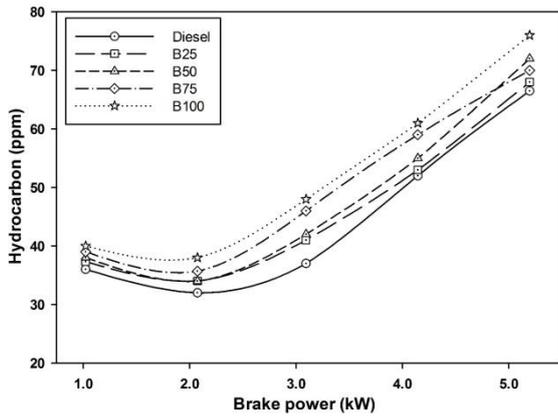


Fig 9. Variations of hydrocarbon Vs brake power

4.6. Heat release rate with crank angle

The variation of heat release rate with respect to crank angle is shown Fig 10. The diesel attaining maximum heat release rate compared to biodiesel blends. This is due to longer the ignition delay period for diesel then biodiesel blends. The biodiesel blends are premixed combustion because maximum heat release rate occurred in the earlier stage of combustion and slow burning compared to diesel fuel. The B25 maximum heat release rate at 107 KJ/m³deg. However diesel reached at 110 KJ/m³deg. Increasing the accumulation of diesel while running achieved longer delay period resulting the higher rate of heat release Sahoo et al [25].

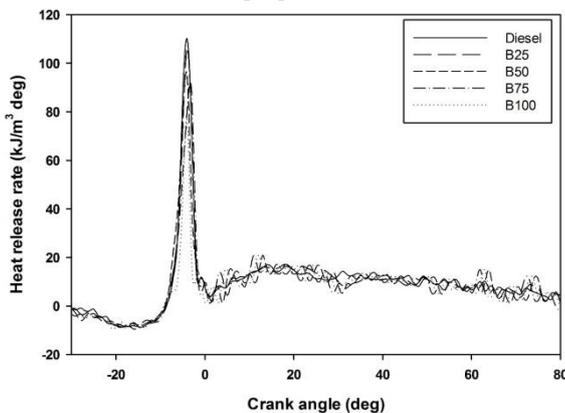


Fig 10. Variations of heat release rate Vs crank angle

4.7. Cylinder pressure

In a compression ignition (CI) engine, the cylinder pressure depends upon the fuel-burning rate during the premixed burning phase. Figure 11 shows the variation of cylinder pressure with respect to crank angle at maximum load. It is seen from the figure that the peak in-cylinder pressure for B100 is noted to be lower than that of B25 by 2.4% due to higher viscosity of biodiesel. However the pressure rise is always higher for diesel and lower in the case of biodiesel operation due to its slower burning characteristics. The premixed combustion phases of B25 blends was envisaged to be closer to diesel. As the blends quantity increases the amount of fuel taking part in the uncontrolled combustion stage of the mixture increases, which results in a higher

pressure rise and the cylinder pressure depends upon burned fuel fraction during the premixed burning phase

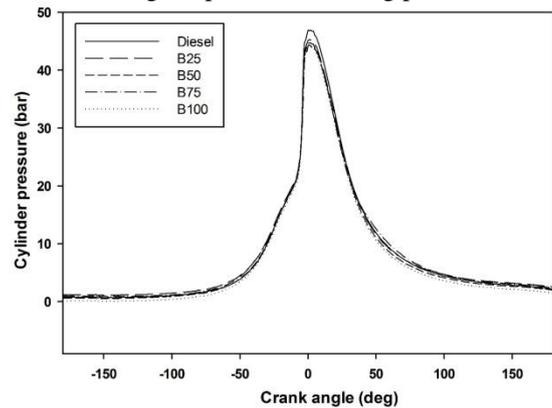


Fig 11. Variation of In-cylinder pressure vs crank angle

5. CONCLUSION

Mahuabiofuel have been produced by catalytic cracking using coal ash as a catalyst and their fuel characteristics have been analyzed. An experimental investigation has been carried out in single cylinder, four stroke, water cooled, and diesel engine. The performance and emission parameters are evaluated. The most important conclusions derived are summarized as follows:

- Biofuel produced from *Mahua* oil and satisfies the ASTM standards and thus can be used as alternative to diesel fuel.
- Based on the result revealing the presence of aluminum, silicon, iron and oxygen in it. Therefore the coal fly ash act as a better catalyst for production of biofuel.
- Cracked biofuel showed increasing the calorific value of fuel and viscosity.
- GCMS showed cracked oil presence of esters, paraffin's, olefins and so on.
- Biofuel has similar combustion characteristics as diesel fuel and biodiesel blends can reduce smoke opacity, oxides of nitrogen but on the other hand carbon monoxide and hydrocarbon increased then diesel at all load.
- CO and HC emission increased with increase in blend percentages and at all tested conditions they were higher than diesel fuel.
- Decreased in NOx emission with increasing the concentration of the *Mahua* blends. The NOx emission of B100 and diesel are 1126 ppm and 636 ppm respectively at full load.

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