
P. V. Rao

Abstract—The aim of the present research work is to investigate the influence of Jatropha biodiesel properties on various characteristics of a direct injection compression ignition engine. The experiments were performed at different engine operating regimes with the injection timing prescribed by the engine manufacturer for diesel fuel. The engine characteristics with Jatropha biodiesel were compared against those obtained using diesel fuel. From the results, it is observed that the biodiesel performance and emissions are lower than that of diesel fuel. However, the NOx emission of Jatropha biodiesel is more than that of diesel fuel. These high NOx emissions are due to the presence of unsaturated fatty acids and the advanced injection caused by the higher bulk modulus (or density) of Jatropha biodiesel.

Furthermore, the possibility for reduction of NOx emissions without expensive engine modifications (hardware) was investigated. Keeping this in mind, the Jatropha biodiesel was preheated. The experimental results show that the retarded injection timing is necessary when using Jatropha biodiesel in order to reduce NOx emission without worsening other engine characteristics. Results also indicate improved performance with the application of preheated biodiesel. The only penalty for using preheated biodiesel is the increase of smoke (soot).

Keywords—chemical properties, combustion, exhaust emissions, Jatropha biodiesel

I. INTRODUCTION

The Direct Injection Compression Ignition (DI-CI) engine has the highest thermal efficiency of any internal combustion engine and therefore produces the least "greenhouse" carbon dioxide (CO₂) from its exhaust. It has, however, a number of disadvantages, including a lower specific output power than the gasoline engine; significant amounts of particulate matter (PM) and oxides of nitrogen (NOx) in the exhaust. NOx and hydrocarbons (HCs) are the precursor pollutants which can combine to form photochemical smog. These exhaust pollutants irritate the eyes and throat, reduces the ability of blood to carry oxygen to the brain and can cause headaches, and also pass deep into the lungs causing respiratory problems for the human beings [1]. Long-term exposure has been linked with leukemia and at high concentrations; it can lead to death [2]. The associated environmental and health risks with diesel exhaust emissions and the reduction targets imposed by increasing stringent emission regulations have resulted in a large number of research studies worldwide over the last decade and this ever increasing stringent emission requirements encourage the use of biodiesel fuels in CI engines.

Till today several biodiesel fuels for CI engines have been investigated. Most investigations show that the use of biodiesel results in lower emissions of carbon monoxide (CO), HC, and smoke, where as the emissions of NOx increases [3]-[6]. The combustion analysis of biodiesel revealed that the NOx emissions were sensitive to the crank angle at which the maximum cylinder temperature and the maximum rate of heat release occurred [7]. A very important factor in engine out NOx emission is the injection timing [8], [9]. Various researchers have shown that the physical properties of density, viscosity, and isothermal compressibility strongly effect injection timing, injection rate and spray characteristics [10]-[12]. Astakhov has reported that the speed of propagation of the pressure pluses generated by the continuous jerk of the pump plunger is a function of the properties of the fuel used [10]. For this reason, the attention in this paper is focused on the possibility of reducing NOx emission when using biodiesel as fuel. To reduce the NOx, the experiments were performed on a DI-CI engine with preheated jatropha biodiesel as fuel.

II. PRODUCTION OF JATROPHA BIODIESEL FROM JATROPHA CURCAS L.

Jatropha curcas L. is a drought resistant annual shrub belongs to the family of Euphorbiaceae [13]. The oil has golden yellow color and is prepared from the seeds of jatropha curcas. These seeds are black in color and oval in shape [14]. Recently there was a renewed interest on the utilization of this
seed oil in view of the relatively high oil content about 66% [15], [16]. This shrub is native to tropical America, but is now cultivated widely in tropical countries throughout the world. Jatropha oil is extremely viscous with a kinematic viscosity about 22 times greater than that of diesel fuel. The properties of the Jatropha oil are shown in Table I.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetane Number</td>
<td>45</td>
</tr>
<tr>
<td>Density@ 15 °C</td>
<td>0.92 g/cm³</td>
</tr>
<tr>
<td>Calorific Value</td>
<td>39.66 MJ/kg</td>
</tr>
<tr>
<td>Flash Point</td>
<td>240 °C</td>
</tr>
<tr>
<td>Pour Point</td>
<td>8 °C</td>
</tr>
<tr>
<td>Viscosity @ 40 °C</td>
<td>49.5 mm²/s</td>
</tr>
<tr>
<td>Carbon Residue</td>
<td>0.44%</td>
</tr>
<tr>
<td>Iodine Value</td>
<td>93 g of I₂/100g</td>
</tr>
<tr>
<td>Water content</td>
<td>822 mg/kg</td>
</tr>
<tr>
<td>Acid Value</td>
<td>2.81 mg of KOH/g</td>
</tr>
<tr>
<td>Free Fatty Acids</td>
<td>38%</td>
</tr>
</tbody>
</table>

The Jatropha biodiesel (JBD) is produced by chemically reacting jatropha oil with an alcohol (methyl or ethyl), in the presence of a catalyst. The free fatty acid (FFA) content is the key parameter for identifying the process of biodiesel preparation. A two-stage process is used for the esterification of the jatropha oil [17]-[19]. The first stage of the process is called esterification, and this is used to reduce the FFA content in jatropha oil by esterification with methanol (99% pure) and acid catalyst (sulfuric acid-98% pure) in one hour reaction at 60 °C. In the second stage, called transesterification, the triglyceride portion of the jatropha oil reacts with methanol and base catalyst (potassium hydroxide-99% pure), in one hour reaction at 65 °C, to form an ester and glycerol. In this process, the triglyceride is converted stepwise to diglyceride, monoglyceride, and finally glycerol as shown in Fig. 1, in the form of chemical reactions.

\[
\text{Triglycerides} + \text{ROH} \rightleftharpoons \text{Diglycerides} + \text{R COOR} \]
\[
\text{Diglycerides} + \text{ROH} \rightleftharpoons \text{Monoglycerides} + \text{R COOR} \]
\[
\text{Monoglycerides} + \text{ROH} \rightleftharpoons \text{Glycerol} + \text{R COOR} \]

Where,
- R' = CH₃
- R' OH = CH₃OH = Methanol
- (RCOOH) = Catalyst (KOH or NaOH)
- R COOR' = R'COOCHR = Methyl Ester
- R'-COOH = Fatty Acid
- R is a mixture of various fatty acid chains

After transesterification, two layers were observed on cooling. The top layer was raw biodiesel and the bottom layer was glycerin. The glycerol layer was separated and the raw fatty acid methyl ester (FAME) was water washed to remove unreacted methoxide by the process of water washing with air-bubbling. It was then heated to remove the water traces to obtain clear biodiesel. This process resulted in 92% yield of the methyl esters. The important aspects of biodiesel production to ensure trouble free operation in CI engines are: complete transesterification reaction, complete (or nearly complete) removal of glycerol, catalyst, alcohol, and FFA’s and failing to remove these, causes biodiesel to fail in one or more fuel standards. Therefore, to have better control over the properties, the biodiesel is prepared in author’s laboratory under careful observation.

### III. CHARACTERIZATION OF DIESEL AND JBD

The measurements of properties of the fuels were carried out according to ASTM D 6751-02 [20]. The specifications and manufacturers of the instruments were given in the following Table II. The effects of the fuel properties on various operational aspects of the diesel engine were discussed as follows:

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM Method</th>
<th>Instrument Make</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>D 1298</td>
<td>Hydrometer</td>
</tr>
<tr>
<td>Flash Point</td>
<td>D 92</td>
<td>Cleveland open cup tester</td>
</tr>
<tr>
<td>Calorific Value</td>
<td>D 240</td>
<td>Bomb calorimeter</td>
</tr>
<tr>
<td>Kinematic Viscosity</td>
<td>D 445</td>
<td>Kinematic viscometer</td>
</tr>
</tbody>
</table>

#### A. Hydrocarbons and Aromatics

Diesel fuel typically contains over 400 distinct types of organic compounds which includes approximately 80% (vol.) of saturated hydrocarbons (primarily paraffin’s-the straight chain HC’s) and 20% of aromatic hydrocarbons (naphthalene’s-the cyclic HC’s and alkyl benzenes). The saturated hydrocarbons include (approximately) 44% of n-Paraffin, 29% of i-Paraffin and 7% of Naphthenes as shown in Fig. 2. The aromatics are a class of hydrocarbon compounds that are characterized by stable chemical structures. The aromatics containing multiple benzene rings are known as polycyclic aromatic hydrocarbons (PAHs). The aromatics include polycyclic aromatic compounds containing 2, 3, 4, and 5 fused benzene rings and the benzene will act as nuclei for the growth undesired soot [21]. Aromatics are considered...
desirable by CI engine operators because they provide greater energy per liter of diesel fuel; however, they may contribute to higher emissions of PM and NOx, and have lower CN [22]. The Jatropha biodiesel contains no aromatic compounds.

Fig. 2 Composition of diesel fuel

B. Carbon Chain

The carbon chain of diesel fuel includes both medium and long carbon chain, which varies from C₈ to C₂₈. That means, the hydrocarbons range in size from eight carbon atoms (C₈) per molecule to twenty eight carbon atoms (C₂₈) per molecule and the peak in the carbon-number distribution occurs at about C₁₃ to C₁₉ [23]. However, the carbon chain (fatty acid compositions) of jatropha includes only the long chain and varies from C₁₄ to C₂₀ and the peak in carbon-number distribution occurs at about C₁₆ to C₁₈ as shown in Fig. 3 [24].

Fig. 3 Carbon number distribution of jatropha and diesel

C. Fatty Acid Composition

The performance of an ester (biodiesel) as diesel fuel depends on the chemical composition of the ester, particularly on the length of carbon chain and the degree of saturation (and unsaturation) of fatty acid molecules. Fatty acids that do not contain double bonds are referred as saturated because they contain maximum number of hydrogen atoms that a carbon molecule can hold. Fatty acids that contain one double bond are called mono-unsaturated fatty acids (MUFAs), while fatty acids that contain two or more double bonds are called as ploy–unsaturated fatty acids (PUFAs). The JBD contains 27.1% of saturated fatty acids (SFA), 40.8% of MUFA and 32.1% of PUFAs as shown in Fig. 4. JBD is a mixture of methyl esters and mainly contains oleic (C₁₈:1)-40.8%, linoliec (C₁₈:2)-32.1%, palmitic (C₁₆:0)-15.6%, and stearic (C₁₈:0)-9.7%, as shown in Fig 5 and their properties are shown in the Table III.

Fig. 4 Saturated and unsaturated fatty acids in jatropha

D. Iodine Value and Unsaturation

Iodine value is expressed in terms of number of centigrams of iodine absorbed per gram sample of biodiesel. The iodine is introduced in JBD to reacts with the double bonds within the fatty acid structure. Therefore, higher the percentage of unsaturation, the larger will be the iodine value [25]. The lower the iodine value, the better the fuel will be as a biodiesel. Iodine values are useful for determination of overall degree of saturation of the oil, which is important for viscosity, and cloud points. Iodine values greater than 50 may result in decreased engine life, but give better viscosity characteristics in cooler conditions [26]. High degrees of unsaturation is not desirable for fuels because their oxidation...
reactions generally found at high temperatures during combustion, may result in irreversible polymerization to plastic-like substances [21]. The iodine value of a JBD is 93 as compared to that of 38 for diesel fuel as shown in Table IV.

### Table III

**PROPERTIES OF FATTY ACID METHYL ESTERS (FAME)**

<table>
<thead>
<tr>
<th>Methyl Ester of Fatty Acid</th>
<th>Molecular Weight (g/mol)</th>
<th>Density (gm/cm³)</th>
<th>Kinematic Viscosity (cSt)</th>
<th>Cetane Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myristic Acid (C14:0)</td>
<td>228.37</td>
<td>0.8622</td>
<td>3.23</td>
<td>66.2</td>
</tr>
<tr>
<td>Palmitic Acid (C16:0)</td>
<td>256.42</td>
<td>0.853</td>
<td>4.32-4.38</td>
<td>74.5</td>
</tr>
<tr>
<td>Stearic Acid (C18:0)</td>
<td>284.48</td>
<td>0.847</td>
<td>4.45-4.51</td>
<td>86.9</td>
</tr>
<tr>
<td>Oleic Acid (C18:1)</td>
<td>282.46</td>
<td>0.895</td>
<td>1.9-6.0</td>
<td>55-59.3</td>
</tr>
<tr>
<td>Linoleic Acid (C18:2)</td>
<td>280.44</td>
<td>0.9</td>
<td>---</td>
<td>38.2-42.2</td>
</tr>
<tr>
<td>Arachidic Acid (C20:0)</td>
<td>304.5</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

### E. Cetane Number

Cetane number (CN) is a prime indicator of the quality of fuel used in CI engines. It is a dimensionless descriptor. It is related to ignition delay (ID) time, i.e., the time that passes between injection of the fuel and onset of ignition. A shorter ID corresponds to a higher CN and vice versa. Biodiesel with high amounts of saturates (that means low IVs) will have a higher CN; while the biodiesel with high amounts of unsaturates (high IVs) will have a low CN.

The straight-chain, saturated hydrocarbons have higher CNs than branched-chain or aromatic compounds of similar molecular weight and number of carbon atoms as shown in Table III. The longer the fatty acid carbon chains and the more saturated the molecules, the higher the CN [27]-[29]. Branching and chain length influence CN. The CN becoming smaller with decreasing chain length and increasing branching.

Diesel fuel contains many n-alkanes, cycloalkanes, as well as alkylbenzenes and various mono and poly aromatic compounds. Aromatic compounds which occur in significant amount in conventional diesel have low CN’s, but their CNs increase with increasing size of n-alkyl side chains [30]-[33]. The key is the long, unbranched chains of fatty acids, which are similar to those of the n-alkanes of good conventional petro-diesel fuel.

Too high or too low a CN can cause operational problems. If a CN is too high, combustion can occur before the fuel and air is properly mixed, resulting in incomplete combustion and smoke. If CN is too low, engine roughness, misfiring, higher air temperatures, slower engine warm-up, and also incomplete combustion occur.

### Table IV

**PROPERTIES OF TEST FUELS IN COMPARISON TO ASTM BIODIESEL STANDARDS**

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Diesel (HC)</th>
<th>JBD (FAME)</th>
<th>Biodiesel ASTM Standards (D6751-02)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon chain</td>
<td>Cn</td>
<td>C12-C18</td>
<td>C14-C20</td>
<td>C16-C22</td>
</tr>
<tr>
<td>Density(ρ)</td>
<td>gm/cc</td>
<td>0.82</td>
<td>0.88</td>
<td>0.87-0.89</td>
</tr>
<tr>
<td>Bulk modulus (β) @ 20 MPa</td>
<td>MPa</td>
<td>1475</td>
<td>1800</td>
<td>---</td>
</tr>
<tr>
<td>Kinematic Viscosity @ 40 °C</td>
<td>cSt</td>
<td>2.25</td>
<td>3.5</td>
<td>1.9-6.0</td>
</tr>
<tr>
<td>Cetane number</td>
<td></td>
<td>---</td>
<td>48</td>
<td>52</td>
</tr>
<tr>
<td>Iodine value</td>
<td>g Iodine/100g</td>
<td>38</td>
<td>93</td>
<td>120 max.</td>
</tr>
<tr>
<td>Oxygen</td>
<td>%</td>
<td>0.3 max</td>
<td>9</td>
<td>11</td>
</tr>
<tr>
<td>Stoichiometric Air-Fuel ratio</td>
<td></td>
<td>14.86</td>
<td>13.9</td>
<td>13.8</td>
</tr>
<tr>
<td>Lower calorific value</td>
<td>kJ/kg</td>
<td>42 500</td>
<td>38 800</td>
<td>37 518</td>
</tr>
<tr>
<td>Sulfur</td>
<td>%</td>
<td>0.25</td>
<td>0</td>
<td>0.05</td>
</tr>
<tr>
<td>Flash point</td>
<td>°C</td>
<td>66</td>
<td>170</td>
<td>130 min.</td>
</tr>
<tr>
<td>Molecular weight</td>
<td></td>
<td>226</td>
<td>277</td>
<td>292</td>
</tr>
<tr>
<td>Color</td>
<td></td>
<td>Light Yellow</td>
<td>Golden Yellow</td>
<td>---</td>
</tr>
</tbody>
</table>

### F. Oxygen, Lower Calorific Value, and Stoichiometric Air-Fuel Ratio

The fuel elements of primary interest to diesel engine combustion are carbon, hydrogen, oxygen, and sulfur. The amount of each of these elements determines the fuel composition, while the location and type of bond making up the fuel molecules determines the fuel structure. The calorific value (or heat of combustion) of a fuel is directly related to its elemental composition.

The diesel fuel made up of a mixture of various hydrocarbon molecules and contain little oxygen (less than 0.3%), while the jatropha biodiesel contain significant amount of oxygen (9%). The structural oxygen content of a fuel...
improves its combustion efficiency due to an increase in the homogeneity of oxygen with the fuel during combustion.

The increase of oxygen in biodiesel is related to the reduction of carbon and hydrogen, causes the lower value of energy content (or calorific value/heat of combustion) of the jatropha biodiesel as compared to that of conventional diesel fuel, because the oxygen is ballast in fuel and carbon and hydrogen are the sources of thermal energy. The lower calorific value (LCV) is applied to internal combustion (IC) engines, which evaluate the losses of heat for the vaporization of water, appeared in the engine exhaust because of the oxidation of hydrogen of the fuel. The heat content of jatropha methyl ester is nearly 91% that of diesel fuel as shown in Table IV. The Stoichiometric air-fuel ratio of jatropha biodiesel will be lower than that of diesel fuel due to presence of oxygen, as a result improvement in combustion efficiency will be ensured [34]-[36].

G. Density and Bulk Modulus
Fuel density has importance in diesel engine performance since the fuel injection system operates on a volume metering system [37]. The jatropha biodiesel has higher density than diesel as shown in Table IV. A fuel with low energy content per liter will cause the engine to produce less peak power; however this high density of biodiesel compensates the lower energy content. The bulk modulus of JBD is more than that of diesel fuel, due to this the pressure waves generated by the pump plunger travels faster from pump end to the injector end, causes premature injection [38]-[45].

H. Molecular Weight
The average molecular weight of the jatropha biodiesel is calculated by considering the weight percent of each fatty acid and their corresponding molecular weights (see Appendix: A). The Table IV, shows the molecular weight of JBD which is greater than that of diesel fuel.

I. Distillation and Boiling Point
Distillation is the progressing boiling off individual components based on differences in boiling points, resulting in a distillation curve of compounds. Boiling point is a key fuel property for biodiesel as is the case for quality control in diesel fuel industry. The boiling range of diesel fuel is 180-340 °C. The jatropha biodiesel contains a fairly homogeneous quantity of straight-chain hydrocarbons with lengths of 16 and 18 carbons; a single boiling point is typically obtained rather than a defined distillation curve [46]. The boiling point of JBD varies between 330-350 °C.

J. Flash Point Temperature
It is the minimum temperature at which the fuel will gives off enough vapors to produce an inflammable mixture (fuel vapor and air) above the fuel surface, when the fuel is heated under standard test conditions. Flash point varies inversely with the fuel’s volatility. The flash point temperature of the jatropha biodiesel is higher than that of conventional diesel, because the jatropha biodiesel do not have the light fractions. The safety of the jatropha biodiesel is ensured due to higher flash point temperature.

K. Viscosity
Viscosity is a measure of the internal fluid friction of fuel to flow, which tends to oppose any dynamic change in the fluid motion. Viscosity is the major reason why jatropha oil is transesterified to methyl ester (or biodiesel). At 30 °C, the viscosity of jatropha oil is about 16 times greater than of conventional diesel. During esterification, the viscosity of jatropha is reduced from 49.5 cSt to 3.5 cSt, which is also greater than the viscosity of conventional diesel (2.25 cSt) at 40 °C as shown in Fig. 6.

Fuel viscosity affects injector lubrication and atomization. Fuels with low viscosity may not provide sufficient lubrication for the precision fit of fuel injection pumps, resulting in leakage or increased wear. If the viscosity is low, the leakage will correspond to a power loss for the engine and if the viscosity is high the injection pump will be unable to supply sufficient fuel to fill the pumping chamber, and again this effect will be a loss in engine power. Fuels with high viscosity tend to form larger droplets on injection which can cause poor combustion, increased exhaust smoke and emissions.

![Fig. 6 KV versus Temperature](image)

From the testing of above properties, it is observed that, the jatropha properties are meeting the specifications of biodiesel standards of the ASTM D6751-02 “Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels” [20]. And the above JBD was found suitable for usage as biodiesel in the DI-CI engine.

IV EXPERIMENTAL TEST RIG AND PROCEDURE
Experiments were carried out on stationary, water cooled, naturally aspirated, 4-stroke, single cylinder, direct injection compression ignition (DI-CI) engine, with the specifications shown in Table V. The layout of the test rig is shown in Fig. 7.

Engine employs the conventional, cam-driven, in-line (Pump-Line-Nozzle) fuel injection system shown in Fig. 8.
This injection system consists of a fuel pump (jerk pump), a fuel discharge tube of length 585 mm (23 inch. approx.), and an injector (or atomizer). A ‘column of fuel’ is formed by (i) pump chamber, (ii) discharge tube, and (iii) the injector. This column of fuel behaves like a stiff spring. The pressure pulse generated by pump plunger propagates through the column of fuel to develop pressure at the nozzle end. When the fuel pressure reached a pressure more than that required to open the needle valve, then the valve is lifted to inject fuel into the cylinder. The injection was performed at a static injection timing (optimum) of 23° BTDC set for diesel fuel. The engine was tested with baseline diesel fuel, and jatropha biodiesel (with and without preheating). For preheating biodiesel fuel; heating devices were placed along the fuel discharge tube.

Experimental engine was instrumented with in-cylinder pressure transducer so that any pressure of interest could be monitored. Water cooled pressure sensor is used for pressure measurement, and Apex innovations, Pune, India, software: C7112 is used to record the combustion pressure in the cylinder. In cylinder pressure and crank angle were recorded using the data acquisition system consisting of PC class computer with data acquisition board. The system was placed with crank shaft encoder at 360 points per engine revolution. The cylinder pressure signal is based on the data acquired during 40 consecutive working cycles of the engine. Thermocouple was placed in the exhaust manifold to measure the temperature of the exhaust gases. Engine performance characteristic parameter were monitored and recorded. All other data necessary for final evolution including air flow, fuel flow, pressures, and temperatures were also recorded. The eddy current dynamometer is used to measure the power (or torque) and brake load was varied in five equal steps.

Thermocouple was placed in the exhaust manifold to measure the temperature of the exhaust gases. Engine performance characteristic parameter were monitored and recorded. All other data necessary for final evolution including air flow, fuel flow, pressures, and temperatures were also recorded. The eddy current dynamometer is used to measure the power (or torque) and brake load was varied in five equal steps.

| TABLE V
<table>
<thead>
<tr>
<th>TEST ENGINE SPECIFICATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engine make and model: Kirloskar-AV1</td>
</tr>
<tr>
<td>Maximum power output: 3.72 kW</td>
</tr>
<tr>
<td>Rated speed (constant): 1500 rpm</td>
</tr>
<tr>
<td>Bore x Stroke: 80 mm x 110 mm</td>
</tr>
<tr>
<td>Compression ratio: 16.5</td>
</tr>
<tr>
<td>Fuel injection system: In-line, direct injection</td>
</tr>
<tr>
<td>Nozzle opening pressure: 205 bar</td>
</tr>
<tr>
<td>Method of cooling: Water cooling</td>
</tr>
<tr>
<td>B.M.E.P @ 1500 rpm: 5.31 bar</td>
</tr>
</tbody>
</table>

Fig. 7 Layout of test rig

Fig. 8 Conventional cam-driven, in-line, jerk-pump fuel injection system

The MRU Exhaust gas analyzer (Make: Germany, Model: Delta 1600 L) is used for measuring gaseous emissions and AVL smoke meter (Make: Graz-Austria, Model: 409 D) is used to measure the soot. The specifications of the emission measuring devices are shown in Table VI

| TABLE VI
<table>
<thead>
<tr>
<th>SPECIFICATIONS OF THE EXHAUST GAS ANALYZER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaseous emissions</td>
</tr>
<tr>
<td>NO</td>
</tr>
<tr>
<td>HC</td>
</tr>
<tr>
<td>CO</td>
</tr>
<tr>
<td>CO2</td>
</tr>
</tbody>
</table>
V THEORY OF COMBUSTION AND NOX FORMATION

Combustion is the process of burning of the fuel in the presence of oxygen to produce heat. The formation of NOx is dependent on the temperatures during the combustion, the amount of O2 and N2 in the charge, and the time available for them to react with each other in the combustion chamber [47]. The combustion process in CI engines is mainly divided into three phases as shown in Fig. 9. The first phase of combustion is called as ignition delay (ID), in which the tiny fuel droplets evaporates and mixes with high temperature (or high pressure) air. The ID period depends mainly on cetane number, and temperatures of fuel and air. The second phase of combustion is called as period of rapid combustion or premixed combustion. In this phase the air-fuel mixture undergoes rapid combustion, therefore the pressure rise is rapid and releases maximum heat flux. The third phase of combustion is called as period controlled combustion. In this period, the fuel droplets injected during the second stage is burns faster with reduced ID due to high temperature and pressure. In this third phase the pressure rise is controlled by the injection rate and the combustion is diffusive mode (see Fig. 9).

![Fig. 9 The Three phases of combustion](image)

**Eqn.(a)**, **Eqn.(b)**, **Eqn.(c)**, **Eqn.(d)**, and **Eqn.(e)**) [47] and this oxidation mechanism is known as Zeldovich mechanism as shown in Figure 10.

![Fig. 10 Oxidation mechanisms (Zeldovich) for NOx formation](image)

NOx production in CI engines is very complex, because it is influenced by many factors and many of these factors interact at different levels. NOx is mainly a function of temperature in the combustion chamber. There are two main combustion characteristics that will determine temperature in the cylinder and thus the NOx emission. These are the combustion timing and the combustion rate. The combustion timing relates to the start of combustion (SOC) relative to the piston position in the cylinder. Early combustion timing causes combustion to occur closer to TDC and perhaps during compression process, increasing pressure, temperature, and the NOx emission.

A number of fuel properties have been shown to effect the emissions of NOx [48]. Fuel properties, such as density, viscosity, sound velocity, bulk modulus, cetane number, oxygen content, and so on, have significant effects on the start of injection, start of combustion, and premixed and diffusion burn peak, and over these on the emissions including NOx [49]. Thermal NOx refers to oxides of nitrogen formed through high temperature oxidation of nitrogen found in air during premixed combustion. The rate of thermal NOx is primarily a function of temperature and the residence time of nitrogan at that temperature. Usually at a temperatures of above 2100 K, the nitrogen and oxygen disassociate and participate in a series of reactions (Eqn.(a), Eqn.(b), Eqn.(c), Eqn.(d), and Eqn.(e)) [47] and this oxidation mechanism is known as Zeldovich mechanism as shown in Figure 10.

The combustion timing in CI engines is mainly affected by the start of injection (SOI), and the ignition delay (ID), which is the time between the SOI and SOC. The ID time is mostly affected by the fuel's CN. The biodiesel has higher CN than PD fuel, therefore shortens ID time and advances the combustion timing. BD fuel also has different physical properties such as higher density, speed of sound, and bulk modulus, which can also lead to an earlier start of injection. Early injection timing and higher CN, advance the combustion timing which tends to increase the NOx. Biodiesel has lower energy content than PD fuel and when a greater volume of fuel is injected to correct for this, some fuel injection pumps will advance the SOI timing, causing an additional increase in NOx emission.

The combustion rate, as indicated by the heat release rate, also has an effect on NOx production. More premixed combustion means a high initial rate of combustion which increases NOx. Premixed combustion corresponds to the fuel that is mixed with air and prepared to burn during the ID period. When this fuel auto ignites it usually burns very quickly. CN and fuel volatility are the two most important properties that determine the combustion rate. High CN and low volatility lowers the combustion rate. A biodiesel with a high CN is expected to shorten the ID period and thus lower the amount of fuel that is involved with the premixed portion of the biodiesel combustion, thus lowering NOx emission.

VI RESULTS AND DISCUSSION

A. Performance

The performance of DI-CI engine was evaluated in terms of fuel consumption (FC), brake specific energy consumption (BSEC), and brake thermal efficiency (BTE), which were discussed as follows:

1. Fuel Consumption
The variation of fuel consumption (FC) with power output is shown in the Fig. 11. For all loads, the FC of JBD is more than that of diesel fuel and at maximum power output the FC for diesel, JBD, and preheated JBD (JBD_PH) are 1.04, 1.23 and 1.19 kg/hr respectively. The JBD contains more percentage of oxygen and consequently less percentage of hydrocarbons and calorific value than that of diesel fuel as shown in Table IV. Therefore, due to lower value of calorific value of JBD, this behavior of more fuel consumption was expected for all power outputs. It is also observed that the fuel consumption decreases with preheating of Jatropha biodiesel and the reason is attributed to the improved combustion caused by increased evaporation and spray characteristics.

2. Brake Thermal Efficiency

Fig. 12 shows the variation of brake thermal efficiency (BTE) with power output. The BTE increases as the output power increases for both the fuels. At full load, the BTE for diesel, JBD and preheated JBD is 30.3%, 28% and 29% respectively. The BTE of preheated JBD is closer to diesel fuel, and the reason is attributed to the increased evaporation of tiny fuel droplets with the surrounding air. According to thermodynamic analysis, the degree of constant volume combustion increases the indicated thermal efficiency for JBD (see Fig. 14). As shown in Fig 16, the premixed combustion of JBD is close to top dead center (TDC) and this behavior is due to early fuel injection caused by the higher bulk modulus of JBD.

3. Brake Specific Energy Consumption

Brake specific energy consumption (BSEC) is an ideal variable, because it is independent of the fuel. The BSEC is the input energy required to develop unit power output. Fig. 13 shows that, the BSEC of JBD is higher at all levels of power output compared to corresponding diesel values and the lowest BSEC are 11881, 12414, and 12857 kJ/kW-hr for diesel, preheated JBD and JBD respectively. This is presumably due to lower value of LCV and higher value of kinematic viscosity of JBD. The results also shows that the BSEC decreases with preheating and the reason is attributed to increase in combustion efficiency due to high rate of evaporation of the preheated JBD.

B. Combustion Analysis

1. Peak Pressures

Fig. 14 shows the variation of cylinder pressure with respect to crank angle at maximum power output of 3.72 kW. It is observed that, the jatropha biodiesel (JBD) is burning close to top dead center (TDC) and the peak pressure is higher than that of diesel fuel; even though the jatropha biodiesel is having lower value of LCV. The reason is attributed to the higher bulk modulus of the JBD. When, a fuel with high density (or high bulk modulus) is injected, the pressure wave travels faster from pump end to nozzle end, through an in-line fuel discharge tube. This causes early lift of needle in the nozzle, causing advanced injection [38]. Hence, the combustion takes place very close to TDC and the peak pressure is high due to existence of smaller cylinder volume near TDC. Therefore the reason for peak pressure is attributed to the combined effect of advanced injection and lower value of heat rejection, which occurs due to prevalence of smaller cylinder volume (or surface area) near TDC.
2. Heat Release Analysis

The heat release analysis of carefully measured cylinder pressure time-history has been used as a diagnostic tool of the combustion process. In the present analysis the formulation is based on the following assumptions:

- The apparent or net heat release process is defined in terms of average properties in a single zone, and thus does not distinguish between burned and unburned zones.
- Fuel vapor and combustible products are treated as a mixture of ideal gases.
- Equilibrium (infinitely fast) thermo-chemistry is assumed.
- The sensible enthalpy from fuel injection is small in comparison to other terms.

Subject to the following assumptions, the first of thermodynamics can be reduced in to the following equation (1), which is used to calculate the net heat release.

\[
\frac{dQ_n}{d\theta} = \frac{1}{\gamma - 1} V dp + \frac{\gamma}{\gamma - 1} p dV
\]  

(1)

The equation (2) is used for heat transferred through the cylinder walls.

\[
\frac{dQ_w}{d\theta} = h_c A (T - T_w)
\]  

(2)

The equation (3) gross heat release is calculated from

\[
\frac{dQ_g}{d\theta} = \frac{dQ_n}{d\theta} + \frac{dQ_w}{d\theta}
\]  

(3)

\[
\gamma(T) = \gamma_{300} + b (T-300)
\]  

(4)

\[
h_c = C_1 V^{-0.06} p^{0.8} T^{-0.4} (u_p+C_2)^{0.8}
\]  

(5)

\[
A(\theta) = \pi (D^2/2) + \pi D \left[ \sqrt{(l^2-x_{off}^2)} \right] - a \cos \theta - \sqrt{(l^2-(x_{off} + a \sin \theta)^2)}
\]

\[
V(\theta, x_{off}) = \pi (D^2/4) \left[ \sqrt{(l^2-x_{off}^2)} \right] - a \cos \theta - \sqrt{(l^2-(x_{off} + a \sin \theta)^2)}
\]

The specific heat ratio ($\gamma$) is defined on a crank angle by crank angle basis. It is subjected to variations in gas temperature, since it captures how the internal energy varies with temperature [50]. This value is determined by using the linear equation (4). The heat transfer rate is calculated using the Woschni heat transfer model [51]. The transfer coefficient is calculated by the following equation (5). The constants are $C_1=13.10^{-3}$ and $C_2=1.4$ proposed by Hohenberg [52].

3. Net Heat Release

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_n$</td>
<td>Net heat release</td>
</tr>
<tr>
<td>$Q_w$</td>
<td>Heat transfer to the cylinder wall</td>
</tr>
<tr>
<td>$Q_g$</td>
<td>gross heat release</td>
</tr>
<tr>
<td>$p$</td>
<td>Instantaneous in-cylinder pressure</td>
</tr>
<tr>
<td>$V$</td>
<td>Instantaneous volume of the cylinder</td>
</tr>
<tr>
<td>$T$</td>
<td>Mean gas temperature</td>
</tr>
<tr>
<td>$T_w$</td>
<td>Cylinder wall temperature</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Instantaneous crank angle</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>ratio of specific heats</td>
</tr>
<tr>
<td>$a$</td>
<td>crank radius</td>
</tr>
<tr>
<td>$l$</td>
<td>connecting rod length</td>
</tr>
<tr>
<td>$x_{off}$</td>
<td>pin-off</td>
</tr>
<tr>
<td>$h_c$</td>
<td>instantaneous convective heat transfer coefficient</td>
</tr>
<tr>
<td>$A$</td>
<td>Instantaneous area through which heat is transferred</td>
</tr>
</tbody>
</table>

TABLE VII

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_n$</td>
<td>Net heat release</td>
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<td>$Q_w$</td>
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<td>$l$</td>
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<td>$A$</td>
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</tr>
</tbody>
</table>
Net heat release rate is the measure of the rate at which the work is done plus the change of internal energy. It represents the energy effectively (apparently) absorbed by the working fluid. Fig. 16 shows the net heat release rate (HRR) at maximum output power. A noticeable change in combustion phases were observed for diesel, JBD and JBD_PH (jatropha biodiesel with preheating). The peak value of premixed combustion is more for JBD, than that of JBD_PH, and the diffusive combustion phase is more for JBD_PH, than that of JBD. This is due to poor mixing of JBD with the surrounding air because of its high viscosity. At the time of ignition delay, more quantity of JBD is accumulated and hence the premixed combustion increases; whereas with JBD_PH less quantity of air-fuel mixture is prepared for combustion. This is due to faster evaporation of the preheated biodiesel. Therefore, more burning occurs in the diffusion phase rather than in the premixed phase. The increase in heat release is mainly due to improved mixing and evaporation of JBD_PH, which leads to complete burning.

4. Gross Heat Release

Gross heat release rate is the measure of chemical energy released by combustion of the fuel. According to thermodynamic analysis, the degree of constant volume combustion increases for the biodiesel (see Fig. 14). Fig. 16 and Fig. 17, shows that a significant improvement in diffused combustion and releases more heat with preheated biodiesel (JBD_PH).

5. Exhaust Gas Temperatures

Temperature of exhaust gases, leaving the cylinder represents the extent of temperature reached in the combustion chamber during combustion. It is observed that, with increasing load the cylinder pressure increases and more amount of fuel is burnt leading to an increase in temperature as shown in Fig. 18. The temperature of exhaust gases is observed to be higher with fossil diesel as compared to JBD for entire range of power output. This is expected as the calorific value (or heat of combustion) of fossil diesel is more than that of JBD; therefore greater amount of heat is released in the combustion chamber leading to higher temperature. Also there is an advanced combustion of JBD due to its higher bulk modulus and cetane number, when compared to diesel. Therefore the heat released by fossil combustion is late by few degrees and thus more heat gets exhausted. Where as the exhaust gas temperature of JBD_PH (preheated JBD) is higher than that of JBD, which indicates increase in diffused combustion due to high rate of evaporation and improved mixing between jatropha biodiesel (preheated) and air. Therefore, as the fuel temperature increases, the ignition delay decreases and the main combustion phase (diffusion controlled combustion) increases, this in turn raises the temperature of exhaust gases.

C. Exhaust Gaseous Emissions

The exhaust gaseous emissions (NOx, HC, CO, CO2 and Soot) of the DI-CI engine are discussed as follows:

1. NOx Emissions

The NOx emissions of diesel and Jatropha biodiesel fuels are plotted in the bar chart shown in the Fig.19. Results show that, for both the fuels, the increased engine load promoting NOx emission. Since the formation of NOx is very sensitive to temperature, these higher loads promote cylinder charge temperature, which is responsible for thermal (or Zeldovich) NOx formation. The Jatropha biodiesel is producing more NOx than diesel. The increase in NOx emission is attributed to the presence of mono-unsaturated (40.8%) and poly-unsaturated (32.1%) fatty acids present in the Jatropha biodiesel as show in Fig. 4. From the Figures 16 and 17, it is
observed that; the higher the peak value of premixed combustion, the larger will be the NOx formation. The production of more NOx with JBD fueling is attributable to an inadvertent advance of fuel injection timing due to higher bulk modulus of compressibility, with the inline-fuel injection system shown in Fig. 8. The bulk modulus of a JBD is 1800 MPa as compared to that of 1475 MPa for diesel as shown in Table IV. Therefore, the higher bulk modulus leads to a more rapid transferal of the pressure wave from fuel-pump end to the fuel-injector needle, causes an earlier needle lift and the earlier needle lift causes an advanced (or early) injection (or combustion), which contributed towards large premixed combustion, responsible for thermal NOx production.

Fig. 19 NOx emission

The fuel spray properties may be altered due to differences in viscosity and surface tension. The spray properties affected may include droplet size, droplet momentum, degree of mixing, penetration, and evaporation. The change in any of these properties might be lead to different relative duration of premixed and diffusive combustion regimes. Since the two burning processes have different emission formation characteristics, the change in spray properties due to preheating of the Jatropha biodiesel leads to reduction in NOx formation. The reason is attributed to reduced intensity of premixed combustion regime (see Fig. 16) due to slightly retarded injection, improved evaporation and improved mixing of preheated JBD.

2. HC Emissions
Fig. 20 shows that, for diesel and Jatropha biodiesel fuel, the unburned hydrocarbons (HC) emissions are showing decreasing trend first and then increasing trend with power output. The reason for higher level of HC at 0 kW power output is attributed to the flame quenching and cooled layer of the charge near the cylinder wall during the cold start. The HC emissions of the Jatropha biodiesel is less than that of diesel fuel. The decrease in CO emission for JBD is attributed to the high cetane number and the presence of oxygen in the molecular structure of the Jatropha biodiesel. Also, the CO emission levels are further reduced for JBD_PH (preheated JBD) and the reason is attributed to its reduced viscosity, density, and increase in rate of evaporation due to preheating.

Fig. 20 HC emission

3. CO Emission
Fig. 21 shows that, for both fuels, the increasing trend of carbon monoxide (CO) emission levels are observed with power output. This increasing trend of CO emissions is due to increase in volumetric fuel consumption and knock with the engine power output. The formation of CO emission mainly depends upon the physical and chemical properties of the fuel used. It is observed that, the CO emission of Jatropha biodiesel is less than that of diesel fuel. The decrease in CO emission for JBD is attributed to the high cetane number and the presence of oxygen in the molecular structure of the jatropha biodiesel. Also, the CO emission levels are further reduced for JBD_PH (preheated JBD) and the reason is attributed to its reduced viscosity, density, and increase in rate of evaporation due to preheating.

Fig. 21 CO emission

4. CO₂ Emission
Fig. 22 shows that, for both fuels, the increasing trend of carbon dioxide (CO₂) emission levels are observed with power output.

Fig. 22 CO₂ emission
output. This increasing trend of CO₂ emissions is due to increase in volumetric fuel consumption. It is observed that, the CO₂ emission of Jatropha biodiesel is less than that of diesel fuel. This is attributed to the presence of oxygen and high cetane number of jatropha biodiesel. However, the CO₂ emission levels are increased for JBD_PH (preheated JBD) and the reason is attributed to more fuel consumption caused by high temperature and improved combustion.

5. Smoke (soot) Density
The results show that, the soot emission increases with power output for both the fuels as shown in Fig. 23. This increasing trend is attributed to the increase in volumetric fuel consumption with the power output.

At lower power outputs (0 kW and 0.93 kW), the JBD showed a slightly higher levels of soot than that of diesel fuel. A portion of the fuel rich mixture may fail to burn was emitted as soot. This reason is attributed to poor quality air-fuel mixing and this poor mixing is due to higher viscosity and density of Jatropha biodiesel. It is also observed that, the diesel fuel at higher power outputs showed a higher level of smoke than that of Jatropha biodiesel (both preheated and unheated). This increase in soot emission is due to the higher boiling point and thermal stability of the aromatic hydrocarbons present in the diesel fuel. Especially the presence of branched and ring (multi-ring or poly) structures of diesel fuel can increase the soot levels. It is also observed that, the Jatropha biodiesel is emitting lower levels of smoke as compared to that of diesel fuel under similar operating conditions. This is probably because of the combined effect of higher cetane number and presence of oxygen in the Jatropha biodiesel, which improves the combustion. The oxygen content in diesel and Jatropha biodiesel is 0.3 % and 9.0 % respectively. Therefore, it is concluded that, the increase of oxygen in the fuel tends to reduce the smoke (soot) emission for all power outputs. However, the smoke emission is increasing for JBD_PH (preheated JBD), as shown in Fig. 23. The reason is attributed to the late phase of combustion, particularly increase in diffusive combustion (heat release) and complete burning of JBD_PH during diffusive combustion mode, as compared to that of JBD.

VII. CONCLUSIONS
The present work confirms the influence of the higher bulk modulus of jatropha biodiesel on combustion timing with the ‘in-line’ fuel injection systems. The advanced combustion timing results increased NOx emission.

The increase in NOx emission of jatropha biodiesel is attributed to the mono (C₁₈:₁) and poly (C₁₈:₂) unsaturated fatty acids.

The performance of the engine is increased when the jatropha biodiesel injected at diesel fuel viscosity. That means, the performance of the engine operating on JBD_PH (preheated JBD) is more than the engine operating on diesel mode.

Decrease in premixed combustion and increase in diffused combustion is observed with preheating of the jatropha biodiesel.

With preheating, the reduction in NOx emission and increase in soot emission is attributed to lower premixed combustion and high diffused combustion respectively.

Except soot all the emissions are reduced with preheating of the jatropha biodiesel.

APPENDIX: A

<table>
<thead>
<tr>
<th>Fatty Acids</th>
<th>Molecular Weight</th>
<th>% of Fatty Acids in Jatropha</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₄:₀</td>
<td>228.38</td>
<td>1.4</td>
<td>3.19</td>
</tr>
<tr>
<td>C₁₆:₀</td>
<td>256.43</td>
<td>15.6</td>
<td>40.0</td>
</tr>
<tr>
<td>C₁₈:₀</td>
<td>284.48</td>
<td>9.7</td>
<td>27.59</td>
</tr>
<tr>
<td>C₁₈:₁</td>
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<td>40.8</td>
<td>115.24</td>
</tr>
<tr>
<td>C₁₈:₂</td>
<td>280.45</td>
<td>32.1</td>
<td>90.02</td>
</tr>
<tr>
<td>C₂₀:₀</td>
<td>312.54</td>
<td>0.4</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Molecular Weight of Jatropha Oil $\sim 277(277.31)$

ACKNOWLEDGMENTS
The author thank Indian Institute of Chemical Technology (IICT), Hyderabad, for providing necessary experimental support and Prof. N Someswara Rao, Department of Analytical Chemistry, Andhra University, for testing the properties of Jatropha biodiesel. This study was supported by TEQIP (Technical Education Quality Improvement Program: First Phase).
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A/Prof. P. V. Rao was born on 15th December 1967, in Selapaka village, East Godavari district of Andhra Pradesh state in India. He obtained Diploma in Automobile Engineering (1984) from Andhra Polytechnic, Kakinada. Degree in Mechanical Engineering (1991) from Andhra University, Visakhapatnam, and Masters Degree in Mechanical Engineering (1993) from Indian Institute of Science, Bangalore, India. He is working in the field of Biodiesel Fuels from the last seven years. Presently, he is working as ASSOCIATE PROFESSOR in the Department of Mechanical Engineering, Andhra University, Visakhapatnam, Andhra Pradesh, India. He has 17 years of teaching experience, and teaching Thermodynamics, IC Engines, and Automobile Engineering for UG and PG students. He has 8 years of research experience. He published two papers in national journals and four papers in international journals. He presented (and published in proceedings) six papers in international refereed conferences like: 40th ACEC (Chemeca 2010, Adelaide), IMechE (Injection Systems for IC Engines, London, 2009), ASME (ICES 2008, Chicago), JSME (COMODIA 2008, Sapporo), and ASPACC 07 (Nagoya). His research interests are IC Engines (Combustion and Exhaust Emissions), Biodiesel Fuels (Preparation and Characterization), and Thermodynamics. He received an Australian Leadership Award (ALA Fellowship Program: The Science and Commercial Application of Biofuels), sponsored by the Federal Government of Australia in 2010.

A/Prof. Rao is a regular member of Society of Automotive Engineers of Japan, life member of the Combustion Institute (Indian Section), and the Institution of Engineers (India), and member of the Indian Science Congress Association. He is awarded with a certificate of merit for his publication in the Journal of Institution of Engineers (India) Journal in 2006.