Biodiesel Exhaust Treatment with HFAC Plasma supported by Red Mud: Study on DeNOx and power consumption

Anusuya Bhattacharyya, B S Rajanikanth*

*Indian Institute of Science, Bangalore 560012, India

Abstract

The concentration of Nitrogen Oxides (NOx) in engines which use biodiesel as fuel is higher compared to conventional diesel engine exhaust. In this paper, an attempt has been made to treat this exhaust using a combination of High frequency AC (HFAC) plasma and an industrial waste, Red Mud which shows proclivity towards Nitrogen dioxide (NO₂) adsorption. The high frequency AC source in combination with the proposed compact double dielectric plasma reactors is relatively more efficient in converting Nitric Oxide (NO) to NO₂. It has been shown that the plasma treated gas enhances the activity of red mud as an adsorbent/catalyst and about 60-72% NOx removal efficiency was observed at a specific energy of 250 J/L. The advantage in this method is the cost effectiveness and abundant availability of the waste red mud in the industry. Further, power estimation studies were carried out using Manley’s equation for the two reactors employed in the experiment and a close agreement between experimental and predicted powers was observed.

1. Introduction

The presence of NOx in diesel engine exhaust is a cause for concern, as it has numerous deleterious effects on the health and environment. Further, improved combustion of fuel in the diesel engine causes this concentration of NOx to increase, owing to the higher combustion temperatures attained within the combustion chamber. Therefore, enhanced fuel efficiency and increased NOx generation seems to go together, thus posing a major challenge in engine design. Recently, fossil fuels are being slowly phased out in favor of natural plant based fuels (also known as biodiesel) [1-4]. The biodiesel is a renewable and environment friendly fuel which is prepared from various plant oils. These fuels, though having less
quantities of Volatile Organic Compounds, tend to have higher levels of NOx [1]. Therefore, finding after-treatment techniques for the treatment of NOx in the exhaust is essential, especially in view of the stringent environmental regulations imposed by worldwide governing bodies on NOx pollution.

One such promising after-treatment technique is the electric discharge based gas cleaning with/ without the support of additives/adsorbents/catalysts [5-9]. The dissociation or conversion of pollutants to non-hazardous gases depends on many parameters in this discharge based cleaning such as oxygen percentage in exhaust, electric field in the treatment zone, voltage profile and other gas parameters. These will eventually decide the inclusion of additives/adsorbents/catalysts in cascade with plasma. In this paper, dielectric barrier discharge plasma generated by HFAC in cascade with industrial waste red mud was used to enhance the efficiency of NOx removal in biodiesel run engine exhaust. The corona electrode used in the reactor is of helical geometry, and is covered by a glass tube to enhance the uniformity of the discharge. Two reactors with similar geometry but slightly different gap distances have been tested and the findings have been reported. The next part of the paper addresses the estimation of power consumed in the plasma reactor as it plays a crucial role in the promotion of this technology. This was carried out using the widely accepted Manley’s equation [10] but with a novel approach so as to facilitate applicability of this equation for complex reactor geometries.

1.1 Experimental set-up

The principle of NOx removal is shown in Fig.1. A 5 kW diesel engine is used to generate the exhaust, a portion of which is sampled for investigation. The main specifications of the engine are: rated speed (1500 rpm), single cylinder, air cooled, cubic capacity (660 cc), compression ratio (15.9:1), fuel consumption (250 g/kWh) The model number is PV-4, class B1, Prakash marketing India Pvt ltd.

The diesel engine was run with 100 % biodiesel fuel obtained from the pongamia pinnata plant seeds, a semi deciduous, nitrogen fixing leguminous tree. The biodiesel was prepared and supplied by the University of Agricultural Sciences, Bangalore. The Pongamia oil mainly consists of fatty acids such as Oleic Acid (50 + %), Linoleic Acid (10 %), palmitic Acid (10 %) and Stearic acid (10%) [2].

Fig.1 Principle of NOx removal

The sampled exhaust was filtered to remove the solid and liquid matter before subjecting it to the plasma treatment, and then goes through the red mud column. The plasma energization is from a 1.2 kHz high frequency HV source.
The plasma reactor consists of two glass dielectrics with a centrally placed helical wire acting as corona electrode. Two such plasma reactors with an annular gap (between the two dielectrics) of 2.5 mm and 3 mm respectively were fabricated and used in these current experiments. They will be referred to as reactor 1 and reactor 2 throughout the paper. The helical wire is of 3 mm pitch, 1 mm thickness and the effective corona region of the reactor was restricted to 4 cm as shown in Fig. 2.

The raw red mud, used as adsorbent in the study, was obtained from the aluminium extraction process in the National Aluminium Company (NALCO), India. It was then processed and converted to pellet from at Central Power Research Institute (CPRI), India. Fig. 3 shows the red mud pellets and table 1 displays its chemical composition [11].

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>12.8</td>
</tr>
<tr>
<td>Al</td>
<td>18.4</td>
</tr>
<tr>
<td>Ti</td>
<td>5.75</td>
</tr>
<tr>
<td>Fe</td>
<td>20.3</td>
</tr>
<tr>
<td>O</td>
<td>43.65</td>
</tr>
</tbody>
</table>

1.2 Power Estimation Methodology

The power consumption of the plasma reactor needs to be estimated in practical applications where the high voltage source capacity is fixed. The Manley’s equation is the widely accepted method to estimate the power consumed within the reactors. However, it has been shown that the Manley’s equation needs to be modified to estimate the power at higher power inputs [12]. Further, knowledge of the inception voltage and capacitance of the plasma reactor is necessary before applying Manley’s equation. However, analytically computing the capacitance for complex reactor geometry, such as ours, is a challenge. In this paper, a semi-empirical approach based on inception voltage and the reactor input power at a voltage slightly higher than the inception voltage was employed to estimate the capacitance of the reactor [11]. The inception voltage is defined as the voltage at which there will be a minimum production of radicals in the gas treatment zone to initiate any chemical reaction. Macroscopically this can be observed as change in the concentration of NO. Using the obtained inception voltage and capacitance values, the Manley’s
equation has been validated at low voltage inputs. At higher voltages, the pattern of power consumption changes, and the Manley’s equation needs to be suitably modified to reflect the actual power [12]. A close agreement between experimental and analytical values has been obtained by this method. The Manley’s expression for power estimation is shown in equation 1 where $C_b$ and $C_g$ refer respectively to dielectric barrier capacitance and the gap capacitance as shown in the equivalent model of plasma discharge. The model also contains a variable discharge resistance which comes into the picture when the discharge is active within the air gap [13].

$$P = 4\pi f V_l \frac{C_b^2}{C_b + C_g} (V_p - V_l)$$

(1)

2. Results and Discussion

In the plasma reactor, the electrical field generated accelerates the electrons preferentially, and these electrons collide with background gas molecules of $O_2$ and $N_2$ to form radicals. The basic reactions leading to $O$, $O_3$ and $N$ radical formation are:

$$O_2 + e \rightarrow O + O + e$$  \hspace{0.5cm} (2)

$$O_2 + O \rightarrow O_3$$  \hspace{0.5cm} (3)

$$N_2 + e \rightarrow N + N + e$$  \hspace{0.5cm} (4)

The radicals so formed react with nitric oxide and nitrogen dioxide leading to their reduction, dissociation or conversion as shown in the following reactions [11].

$$N + O_2 \rightarrow NO + O$$  \hspace{0.5cm} (5)

$$N + O_3 \rightarrow NO + O_2$$  \hspace{0.5cm} (6)

$$O + NO_2 \rightarrow NO + O_2$$  \hspace{0.5cm} (7)

$$NO + O \rightarrow NO_2$$  \hspace{0.5cm} (8)

$$NO + O_3 \rightarrow NO_2 + O_2$$  \hspace{0.5cm} (9)

$$NO + NO_3 \rightarrow NO_2 + NO_2$$  \hspace{0.5cm} (10)

$$NO + N \rightarrow N_2 + O$$  \hspace{0.5cm} (11)

$$NO_2 + O \rightarrow NO + O_2$$  \hspace{0.5cm} (12)

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$  \hspace{0.5cm} (13)

$$NO_2 + NO_3 \rightarrow N_2O_5$$  \hspace{0.5cm} (14)

$$NO_2 + N \rightarrow N_2O + O$$  \hspace{0.5cm} (15)

The presence of hydrocarbons such as ethylene, the alkyl ($C_nH_{2n+1}$), alkoxy ($C_nH_{2n+1}O$) and acyl ($C_nH_{2n+1}CO$) radicals in the exhaust also gives rise to a number of other reactions which facilitate the removal of NOx as shown in reactions 16 and 17 [6].

$$CH_2O_2 + NO \rightarrow NO_2 + CH_2O$$  \hspace{0.5cm} (16)

$$CH_2O + NO \rightarrow HNO_2 + CH_2O$$  \hspace{0.5cm} (17)

The experiments were done with the diesel engine loaded at 20 % of full load capacity. The initial concentration of the relevant exhaust components are given in the table 2. The flow rate of the gas was 6 lpm.
Table 2

<table>
<thead>
<tr>
<th>Exhaust component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx</td>
<td>575 ppm</td>
</tr>
<tr>
<td>NO</td>
<td>540 ppm</td>
</tr>
<tr>
<td>NO₂</td>
<td>35 ppm</td>
</tr>
<tr>
<td>O₂</td>
<td>16.6 %</td>
</tr>
</tbody>
</table>

The Fig. 4(a) shows the NO removal from the exhaust when treated with high frequency AC plasma in the two reactors, with and without the cascaded red mud. It is evident from the graph that reactor 2 performs marginally better than reactor 1, and the presence of red mud enhances the NO removal to some extent. Fig. 4(b) displays the NO₂ variation. It is evident from this graph that most of the decrease in NO in Fig. 4(a) within the plasma reactor alone is actually a result of conversion to NO₂, which is the natural consequence of the highly oxidizing plasma atmosphere. However, we see that with the addition of the red mud column after the plasma reactor, the concentration of NO₂ decreases to a great extent.

A careful observation of the NO removal also reveals yet another interesting fact, which is that the efficiency of the red mud in trapping NO is also enhanced once the exhaust passes through the plasma atmosphere. This can be attributed to the combination of chemical reactions with the nitrate esters in the presence of TiO₂ photo-catalyst present in the red mud [14]. The concentration of Ti in our particular sample was found to be around 5.75 % as shown in Fig. 3. Further, the presence of SiO₂ along with TiO₂ in the red mud has contributed for the photo-catalytic activity of TiO₂ under visible light. [15]. The following reaction, therefore, may have contributed for the decrease of NO₂ under the presence of methyl nitrate / methyl nitrite, which were formed during the plasma treatment.

**TiO₂ Catalyst**

\[
2\text{NO₂} + 8\text{CH₃NO₃} \rightarrow 5\text{N₂} + 8\text{CO₂} + 12\text{H₂O} \quad (18)
\]

**TiO₂ Catalyst**

\[
6\text{NO₂} + 8\text{CH₃NO₂} \rightarrow 7\text{N₂} + 8\text{CO₂} + 12\text{H₂O} \quad (19)
\]
The NOx removal efficiency of both the reactors with the cascaded red mud can be viewed from Fig 5. The reactor 1 achieves an efficiency of around 61%, and the reactor 2 gives an efficiency of around 72%. The specific energy consumed is similar for both the reactors.

![Fig.5 DeNOx Efficiency of the plasma red-mud combination for reactors 1 and 2](image)

An estimation of this specific energy is essential for designing future reactors, and it is to satisfy this need the Manley’s equation was devised [10]. As mentioned in section 1.2, to utilize Manley’s equation to estimate the power and subsequently the specific energy, it is essential to know the corona inception voltage and the capacitance of the plasma reactor. The inception voltage is identified by the procedure outlined in section 1.2, and then the capacitance of the plasma reactor is back calculated by measuring the power corresponding to a voltage slightly higher than the inception voltage, and substituting into the Manley’s equation to find the capacitance. This is essential in this case as the plasma reactor geometry is too complicated to use simple analytical expressions. Further, direct measurement of capacitance methods often include ground and stray capacitances which distort the actual capacitance value. Hence, this method has been proposed.

![Fig.6 Actual and estimated powers for the plasma reactors (a) Reactor 1 (b) Reactor 2](image)
The capacitance of reactor 1 and 2 obtained by this method was found to be 0.4500 nF and 4533 nF respectively. The inception voltage for both the reactors was found to be close to 10 kV.

However, it was noticed that the Manley’s equation was able to predict the power only up to a certain voltage levels beyond which due to the cascading effect of surface and voluminous discharges present in the innermost dielectric tube and glow type discharge present in the outer dielectric tube leading to abrupt increase in the power as seen in fig.6. Further, such abrupt power increases are reactor specific. Therefore, the Manley’s equation needs to be modified at higher voltages for a particular reactor geometry [12]. Basically the methodology involves in extrapolating the slopes for the two segments of the graph at the point of abrupt increase in power. The intersection of the slopes on the voltage axis is then taken for calculation of a correction factor which is incorporated into the Manley’s equation. In the present case the respective factors for reactor 1 and 2 are 15.08 and 13.4. The modified manley’s equation for reactor 1 will then be (applicable for \( V > 15.5 \text{kVp} \))

\[
= 15.08f_V \frac{C_b^2}{C_b + C_g} \left( V_p - 1.4313V_i \right)
\]  

(20)

and for reactor 2 it will be (applicable for \( V > 14 \text{kVp} \))

\[
= 13.4f_V \frac{C_b^2}{C_b + C_g} \left( V_p - 1.295V_i \right)
\]  

(21)

The Figs. 6 (a) and (b) show the estimated and actual power which are in close agreement. Now that for a given reactor, we have one set of experimentally measured power values and an equivalent set of power values derived from modified Manley’s equation, it should be possible to estimate the power at different values of frequencies and higher voltage values not covered in the experiment. This is the basic idea in deriving the equations 3 and 4. A detailed validation of the equations for different parametric variations will be taken up shortly.

3. Conclusion

In this paper, High Frequency AC plasma was utilized for cleaning biodiesel exhaust. The DeNOx efficiencies with two plasma reactors with similar geometries but slightly different annular gap distances were analysed. It was found that the first reactor, having a gap length of 3.11 mm, achieved an NOx removal efficiency of 61% and the other, having a gap length of 2.8 mm, displayed an efficiency of 72%, more or less similar to the first reactor. The power consumption characteristics of the two reactors were then studied and a a semi-empirical approach was proposed to predict the capacitance and subsequently the powers based on modified Manley’s equation.

Acknowledgements

We thank the National Aluminium Corporation, India for providing the raw red mud and Central Power Research Institute of India for the preparation of the red mud pellets.

References


Biography

Anusuya Bhattacharyya was born in Chennai, India in 1987. She received her B.E. degree in electrical engineering from Anna University, Chennai, in 2009 and MS from Indian Institute of Science, Bangalore, in 2013 where she is currently pursuing her PhD. Her main research is in the application of electrical discharges for diesel exhaust cleaning.

B.S. Rajanikanth was born in Bangalore in 1965, (S’93-M’95-SM’00). He received the B.E. degree in electrical engineering from Bangalore University in 1987 and the M.S. and Ph.D. degrees in HV engineering from IISc, Bangalore, in 1990 and 1993, respectively. He is currently a Professor of Electrical Engineering Department, IISc, Bangalore. His research interests are mainly in the applications of High voltage to air pollution control and modeling of electrical characteristics of precipitators. He has several publications in journals and international conferences. Two of his papers on air pollution control have received IEEE committee paper awards.