STUDIES ON CONTROL OF ALDEHYDES FROM FOUR STROKE COPPER
COATED SPARK IGNITION ENGINE WITH METHANOL BLENDED
GASOLINE WITH IMPROVED DESIGN OF CATALYTIC CONVERTER

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ABSTRACT

Investigations were carried out to study aldehyde emissions (formaldehyde and acetaldehyde) of a variable speed, variable compression ratio, four–stroke, single–cylinder, spark ignition (SI) engine having copper coated engine [CCE, copper–(thickness, 300 µ) coated on piston crown and inner side of cylinder head] provided with catalytic converter with different catalysts of sponge iron and manganese ore with methanol blended gasoline (80% gasoline and 20% methanol by volume) and compared with conventional engine (CE) with pure gasoline operation. Dinitrophenyl hydrazine (DNPH) method was employed for measuring aldehydes. The engine was provided with catalytic converter with sponge iron and manganese ore as catalysts. There was provision for injection of air into the catalytic converter. The performance of the catalyst was compared with one over the other. The engine with copper coated combustion chamber decreased aldehyde emissions effectively in comparison with engine with conventional combustion chamber. Catalytic converter with air injection significantly reduced pollutants with different test fuels on both configurations of the combustion chamber. Catalytic converter with improved design reduced aldehyde emissions effectively when compared with existing design.

Keywords: SI Engine; Methanol Blend; CE; CCE; Aldehyde Emissions; Catalytic converter and air injection.

1. INTRODUCTION

In the scenario of fast depletion of fossil fuels, ever increase of pollution levels with fossil fuels and increase of burden on developing countries like India, the search for alternative fuels has
become pertinent apart from effective fuel utilization which has been the concern of the engine manufacturers, users and researchers involved in combustion & alternate fuel research.

Alcohols (ethanol and methanol) are important substitutes for gasoline fuel in SI engine, as their properties are comparable to gasoline fuel. That too their octane ratings are very high. If alcohols are blended in small quantities with gasoline fuel, no engine modification is necessary. Methanol has higher C/H (C= Number of carbon atoms, H= Number of hydrogen atoms) ratio which leads to form water vapor during combustion. It has oxygen molecule in its composition. Theoretical air fuel ratios are less for methanol when compared with gasoline operation. Hence methanol blended with gasoline can be effectively used as fuel in SI engine.

If the engine is run with alcohol, aldehydes are also to be checked. These aldehydes are carcinogenic in nature and once they are inhaled, cause severe headache and vomiting sensation. [1–3]. Aldehyde vapors effects on human health include irritation of eye, throat, nose, asthma, pulmonary function. Thresholds for sensory irritation determined by controlled exposure studies, are reported as 0.6-1.2 mg/m$^3$ [0.5-1.0 ppm] (formaldehyde) and 90 mg/m$^3$ [50 ppm] (acetaldehyde) [4]. These levels are substantially higher than the generally reported ambient air concentrations of these vapors. Aldehydes are partially oxygenated organic compounds containing carbonyl group. An aldehyde functional group consists of a carbon atom bonded to a hydrogen atom double-bonded to an oxygen atom (O=CH–). Control of aldehyde emissions in SI engines was not sufficiently reported in literature. Hence control of these emissions is immediate and an urgent task.

There are many methods to control aldehyde emissions from the engine, out of which engine modification and provision of catalytic converter to the engine are simple techniques. Copper is coated on piston crown and inner side of cylinder head as improves pre–flame reactions and combustion stabilization, because copper is a good conductor of heat [5–7].

Reduction of aldehyde emissions from engine depends on mass of the catalyst, void ratio (defined as ratio of the volume of the catalyst to the volume of catalytic chamber), temperature of the catalyst, air flow rate, speed and compression ratio of the engine [8–11]. Investigations were conducted with alcohols (ethanol and methanol) in CE and engine with copper coated combustion chamber so as to improve the performance of the engine [12–13]. However, no systematic studies were available on control of aldehyde emissions from engine with copper coated combustion chamber with the use of gasoline blended with ethanol with improved design of catalytic converter with different catalysts.

The present paper reported the control of aldehyde emissions with different test fuels of pure gasoline and methanol blended gasoline (gasoline 80% and methanol 20% by volume) with improved design of catalytic converter with different catalysts of sponge iron and manganese ore and the performance of the catalyst was compared with one over the other.

2. MATERIAL AND METHOD

2.1. Fabrication of copper coated combustion chamber

In catalytic coated engine, piston crown and inner surface of cylinder head were coated with copper by flame spray gun. The surface of the components to be coated were cleaned and subjected to sand blasting. The material to be coated, which is either in the form of wire, rod or fine powder, was fed to a melting zone. The molten metal was further heated to a very high temperature leading to plasma stage. The hot plasma is accelerated along with carrier gas in the form of a jet towards the substrate. When the plasma impinges on the surface to be coated, the coating material flattens and sticks to the surface. It forms a hard surface when it is cooled and coalesced. The plasma coating consists of a spray gun, feed hopper, carrier gas supply unit and power supply unit. The spray gun is used to coat the material of the surface. The coating was applied in layers until the desired thickness was obtained. A bond coating of nickel- cobalt- chromium of thickness 100 microns was sprayed
over which copper (89.5%), aluminium (9.5%) and iron (1%) alloy of thickness 300 microns was coated with METCO (A trade name) flame spray gun. The coating has very high bond strength and does not wear off even after 50 h of operation [5].

2.2. Four stroke copper coated spark ignition engine

Fig.1 shows the schematic diagram of experimental set-up used for investigations. It is a four–stroke, variable speed (2200–3000 rpm), variable compression ratio (3:1–9:1), single-cylinder, water-cooled, SI engine (brake power 2.2 kW, at the speed 3000 rpm) was coupled to an eddy current dynamometer for measuring its brake power. Dynamometer was loaded by a loading rheostat. The accuracy of engine load was ±0.2kW. The bore of the engine was 70 mm while the stroke was 66 mm. Compression ratio of engine was varied with change of clearance volume by adjustment of cylinder head, threaded to cylinder of the engine. Brake power at different percentages of load was calculated by knowing the values of the output signals (voltmeter reading and ammeter reading) of dynamometer and speed of the engine. The accuracies obtained with measurement of output signals of dynamometer were within the limits. The speed of the engine was measured with digital tachometer with accuracy ±1%. Percentage error obtained with measurement of fuel flow rate assuming laminar film in the burette was within the limit.

Air-consumption of the engine was obtained with an aid of air box, orifice flow meter and U-tube water manometer assembly. By means of orifice flow meter and U–tube water manometer, discharge of air was calculated, from which mass flow rate of air was calculated. Percentage error obtained with measurement of difference of water levels in U–tube water manometer assuming laminar film in the manometer was within the limit. Air box with diaphragm was used to damp out the pulsations produced by the engine, for ensuring a steady flow of air through the intake manifold. Coolant water jacket inlet temperature, outlet jacket temperature and exhaust gas temperature were measured by employing iron and iron–constantan thermocouples connected to analogue temperature indicators. The accuracies of analogue temperature indicators are ±1%.

![Fig.1: Schematic Diagram of experimental set-up for four–stroke SI engine](image)
2.3. Measurement of exhaust emissions

DNPH method (dinitrophenyl hydrazine) [8] was employed for measuring aldehydes in the experimentation. The exhaust of the engine was bubbled through 2.4 DNPH solution. The controlled flow rate (2l/m) was maintained by rotometer and then it was purified by means of filter, and then heated to 140° C with heater before sending it to DNPH solution. The hydrazones formed were extracted into chloroform and were analyzed by employing high performance liquid chromatography (HPLC) to find the percentage concentration of formaldehyde and acetaldehyde in the exhaust of the engine. The advantage of this method over other methods is it can simultaneously measure formaldehydes and acetaldehydes.

2.4. Catalytic Converter

A catalytic converter (Fig.2) was fitted to exhaust pipe of engine. Using mild steel, hollow cylinders were made and chemically cleaned with a solution of 10% sodium hydroxide and then with 5% nitric acid and finally dried. For the preparation of catalytically active coating, aluminium oxide was used as the oxidizing catalyst. Kaolinite is clay mineral with the composition of Al₂SiO₅(OH)₄, high temperature RTV silicone, bentonite clay and gel solutions consisting of tetra ethyl ortho silane and ethanol were used as the binders. The finely powdered catalyst and chosen binder were intimately mixed and slurry was made by mixing with a suitable solvent. The hollow cylinders mentioned above were dip coated by dipping in the above slurry solution and then dried. In order to improve the adhesion of coating, an under coat of slurry of above mentioned binders in a suitable solvent was first applied on the cylinders, dried and then the catalytic coating was applied over the under coat. After drying, the adhesion of the catalytic coating was tested by manual abrasion of the coatings. Aluminium oxide of thickness 500 microns was coated on inside portion of catalytic converter. Holes of size 25 mm were provided on circumference of intermediate cylinder and inner cylinder. However, aluminum coating was not provided and holes of size 20 mm were provided on cylinders in previous studies [10]. Holes were made larger in order to ensure proper contact of exhaust gases with catalysts of sponge iron/manganese ore which were less expensive and easily available with low initial cost.

![Fig.2: Details of catalytic converter](image)

Discharge of the engine was calculated from which diameter of the opening through which exhaust gases enter into the catalytic chamber was determined assuming the velocity of exhaust gases (3–4 m/s). The length of the chamber was determined calculating the pressure drop. [14].

Provision was also made to inject a definite quantity of air (60 l/m) into catalytic converter. Air quantity drawn from compressor and injected into converter was kept constant so that backpressure does not increase. If necessary, provision was also made to heat injected air by means of heater (Part No.21).

Experiments were carried out under different operating conditions of catalytic converter like set–A, without catalytic converter and without air injection; set–B, with catalytic converter and without air injection; and set–C, with catalytic converter and with air injection by operating direction valve (Part No.18).

2.5 Manufacturing of methanol

Methanol is produced from organic materials such as grains, fruit, wood and even municipal solid wastes and waste or specifically grown biomass. The municipal solid wastes can be converted to alcohol. The wastes are first shredded and then passed under a magnet to remove ferrous materials. The iron free wastes are then gasified with oxygen. The product synthesis gas is cleaned by water scrubbing and other means to remove any particulates, entrained oils, H2 S and CO2. CO-shift conversion for H2 / CO / CO2 ratio adjustment, alcohol synthesis, and alcohol purification are accomplished. Ethanol is renewable in nature. They have oxygen in their molecular composition. They have low C/H value. It has a low stochiometric air fuel ratio. Its properties are suitable as blended fuel in spark ignition engine.

The properties of test fuels are shown in Table.1. [15]. However, the excess vapor pressure as noticed from Table.1 with alcohol blends can lead to vapor problems (drivability problems), difficulties with hot starts, stalling, hesitation, and poor acceleration. It is possible to add high vapor pressure liquids or gases such as butane either generally or preferably during cold start situations. Either gasoline or LPG could be injected at cold starts to accomplish the same effect.

<table>
<thead>
<tr>
<th>Property</th>
<th>Test Fuel</th>
<th>Test Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Calorific Value (MJ/kg)</td>
<td>Gasoline</td>
<td>M-20</td>
</tr>
<tr>
<td></td>
<td>44.133</td>
<td>38.233</td>
</tr>
<tr>
<td>Reid vapor pressure (kPa)</td>
<td>35.00</td>
<td>66.58</td>
</tr>
<tr>
<td>Research Octane Number</td>
<td>84.8</td>
<td>94.4</td>
</tr>
<tr>
<td>Density at 15.5ºC (kg/l)</td>
<td>0.7678</td>
<td>0.7707</td>
</tr>
<tr>
<td>Latent Heat of Evaporation (kJ/kg)</td>
<td>600</td>
<td>700</td>
</tr>
<tr>
<td>at 15.5ºC</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.6 Operating conditions

Test fuels used in the experimentation were pure gasoline, methanol blended gasoline (methanol 20% by volume blended with gasoline). Different combustion chambers used in the investigations were conventional engine combustion chamber and copper coated combustion chamber. Different operating conditions of catalytic converter were Set–A (without catalytic converter and without air injection), Set–B (with catalyst and without air injection) and Set–C (with catalyst and with air injection).
Void ratio was maintained as 0.7 for sponge iron and manganese ore in order to obtain minimum pollution levels [10]. Air flow rate was maintained as 60 l/m, for minimum pollution levels. Mass of the sponge iron was kept as 2.0, while mass of the manganese ore 2.5 kg [10]. The engine was started and allowed to warm up for a period of 20–30 min. Before running the engine with a new fuel blend, it was allowed to run for sufficient time to consume the remaining fuel from the previous experiment. All the blends were tested under same speed.

3. RESULTS AND DISCUSSION

These aldehydes are responsible for pungent smell of the engine and affect the human beings when inhaled in the large quantities. The volatile aldehydes are eye and respiratory tract irritants. Though Government legislation has not been pronounced regarding the control of aldehyde emissions, when more and more alcohol engines are coming to existence, severe measures the controlling of aldehydes emitted out through the exhaust of the alcohol run engines will have to be taken as serious view.

It is observed from Table.2, that formaldehyde emissions were higher with methanol blended gasoline operation in both versions of the combustion chamber. This was due to oxidation reaction of ethanol with hydro–carbon fuels. This was due to partial oxidation compared to pure gasoline. The low combustion temperature lead to produce partially oxidized carbonyl (aldehyde) compounds with ethanol blended gasoline.

Formaldehyde emissions were quiet low with non-alcoholic fuels with engine with copper coated combustion chamber as noticed from the same table.

From Table.2, it is observed that, with pure gasoline operation, copper coated combustion chamber with Set–A operation of the catalytic chamber (existing) with sponge iron as catalyst decreased formaldehyde emissions by 30% in comparison with engine with conventional combustion chamber. This was due to improved combustion with copper coated combustion chamber due to catalytic activity when compared with engine with conventional combustion chamber.

From table, it is noticed that, with methanol blended gasoline operation, copper coated combustion chamber with Set–A operation of the catalytic chamber (existing) with sponge iron as catalyst decreased formaldehyde emissions by 25% in comparison with engine with conventional combustion chamber. This was due to reduction of intermediate compounds during combustion with copper coated combustion chamber due to pronounced catalytic activity when compared with engine with conventional combustion chamber. Trends were matching well with those of Reference [10].

Set–B operation of the catalytic converter with sponge iron as catalyst decreased formaldehyde emissions by 30% when compared with Set–A operation with test fuels. This was due to improved oxidation reaction of the catalyst. Set–C operation of the catalytic converter with sponge iron as catalyst decreased formaldehyde emissions by 70% when compared with Set–A condition of the catalytic converter. Sponge iron was proved to be efficient in reducing formaldehyde emissions due to its large surface area. Similar trends were observed by Reference [10].

As mentioned earlier in Article.2.4, catalytic converter was redesigned in Article.2.4. Set–B operation of the catalytic converter with sponge iron as catalyst decreased formaldehyde emissions further by 15% and Set–C operation by 20% when compared with existing catalytic converter. This was due to combined effect of improved oxidation reaction of the catalyst and aluminium coating on inner portion of the catalytic chamber.

From Table.2, it is noticed that acetaldehyde emissions followed the similar trends with data of formaldehyde emissions in both versions of the combustion chamber. These emissions decreased considerably with Set–B operation with both versions of the combustion chamber with test fuels. Set–C operation further decreased these emissions with test fuels in both versions of the combustion chamber. However, methanol blended gasoline increased acetaldehyde emissions drastically when
compared with gasoline operation on both versions of the combustion chamber. However, engine with copper coated combustion chamber decreased acetaldehyde emissions in comparison with CE with test fuels. This was due to improved combustion so that intermediate compounds will not be formed. Similar trends were observed by Reference [10]. Sponge iron was proved to be efficient in reducing acetaldehyde emissions due to its large surface area.

As mentioned earlier in Article 2.4, catalytic converter was redesigned. Set–B operation of the catalytic converter with sponge iron as catalyst decreased acetaldehyde emissions further by 15% and Set–C operation by 20% when compared with existing catalytic converter. This was due to combined effect of improved oxidation reaction of the catalyst and aluminium coating on inner portion of the catalytic chamber.

Table 2: Data of Aldehydes emissions in four-stroke SI engine with test fuels at different operating conditions of catalytic converter

<table>
<thead>
<tr>
<th>Emissions/ Catalyst Converter</th>
<th>Set</th>
<th>Pure gasoline operation (Existing)</th>
<th>Methanol blended gasoline (Existing)</th>
<th>Methanol blended gasoline (Modified)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CE</td>
<td>CCE</td>
<td>CE</td>
</tr>
<tr>
<td>Formaldehyde (% Concentration)</td>
<td>Set-A</td>
<td>Sponge iron 6.5 4.5 4.5 10.0</td>
<td>Mn ore 6.5 4.5 4.5 10.0</td>
<td>Sponge iron 3.8 2.1 2.5 6.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Set-B 4.5 4.9 2.5 2.9 7.3 7.8</td>
<td>3.4 3.9</td>
<td>Set-C 2.0 2.4 1.2 1.5 3.6 3.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Set-C 2.5 2.9 1.5 1.9 4.2 4.6</td>
<td>2.3 2.7</td>
<td></td>
</tr>
<tr>
<td>Acetaldehyde (% Concentration)</td>
<td>Set-A</td>
<td>Sponge iron 5.5 3.5 3.5 10.0</td>
<td>Mn ore 5.5 3.5 3.5 10.0</td>
<td>Sponge iron 2.8 2.1 2.4 5.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Set-B 3.5 4.0 2.5 2.7 7.0 7.5</td>
<td>4.9 5.4</td>
<td>Set-C 1.5 1.9 1.0 1.2 3.7 4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Set-C 1.5 1.9 1.0 1.2 3.7 4.0</td>
<td>2.9 3.4</td>
<td></td>
</tr>
</tbody>
</table>

When compared with acetaldehyde emissions, formaldehyde emissions were observed to be higher with methanol blended gasoline operation on both versions of the combustion chamber. This was due to participation of single carbon atom of methanol (CH3OH) with gasoline in chemical reaction forming formaldehyde group (CH2-O).

4. SUMMARY

1. Methanol blended gasoline operation on both versions of the combustion chamber increased aldehyde (formaldehyde and acetaldehyde) emissions, when compared with pure gasoline operation.
2. Engine with copper coated combustion chamber decreased aldehyde emissions by 30% with set–A operation when compared with engine with conventional combustion chamber with test fuels.
3. Set–B operation of the catalytic converter decreased the aldehyde emissions by 40%, while Set–C by 70% with test fuels when compared with Set–A operation.
4. Aldehyde emissions reduced further by 15% with Set-B operation and 20% with Set-C operation with improved design of catalytic converter when compared with existing design. Sponge iron was found to be more suitable in reducing exhaust emission in comparison with manganese ore.

4.1 Research findings
Formaldehyde emissions and acetaldehyde emissions from SI engine were measured by DNPH method. They were controlled by adopting change of design of combustion chamber and with provision of the catalytic converter.

4.2 Future scope of work
Spark plug timings can be varied to reduce the aldehyde emissions. Nano–materials can be tried for catalytic converter.

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REFERENCES OF LITERATURE


