Design and Empirical Inquisition of Catalytic Combustor for Methanol Steam Reformer in HT-PEM Fuel Cell Systems

Abhijeet Chougule, Ramakrishna R. Sonde

Abstract: Steam reforming of methanol is a basic endothermic reaction. For which, a separate external system is required for generation of heat. The reaction speeds are controlled by operating temperature and heat transfer rate to the reactor. This operating temperature has a very narrow window of operation. It is therefore extremely important to have a system that generates controlled combustion based stable heat for providing required heat to reformer.

A design of catalytic combustor was developed and analyzed for methanol steam reformer. The packed bed of combustion catalyst provides active sites for combustion of the methanol water mixture during start-up and later for combustion of anode exhaust gas (AEG) during normal operation. The combustion reactions and their thermodynamics were studied for commercial catalyst. System design was simulated using Engineering Equation Solver (EES) software for determining the quantity of air required for combustion of fuel as well as for dilution of gases to maintain a temperature of 573 K. The design was analyzed using ANSYS DISCOVERY LIVE for understanding the different operating condition(s) inside the combustor. It was also used to generate design of experiments to evaluate, build and demonstrate a catalytic combustor for on-board reformer for HT-PEM fuel cell system.

Keywords: Catalytic combustor, HT-PEM Fuel cell, Hydrogen generation, Methanol steam reformer, On-board reformer, Packed bed, Simulation.

I. INTRODUCTION

Methanol (Chemical formula: CH$_3$OH) is a single carbon-based organic compound which can be produced/derived from fuels such as coal, biomass and natural gas. As per date reported in [1][2], Methanol is finding increasing acceptance as low carbon/carbon neutral fuel. It is an efficient and less polluting fuel with octane number 100, lesser emission of NO$_x$, particulate matter and no emission of SO$_x$. One of the important roles of methanol is in production of hydrogen for fuel cells. Hydrogen is the preferred fuel for fuel cell systems to get the best performance, but gaseous hydrogen is difficult to handle and store. It is therefore very attractive to use a material which can act as hydrogen-carrier or “absorb” the hydrogen. Methanol is an excellent hydrogen-carrier and thus can be used as a fuel that stores hydrogen in liquid form for fuel cells. Hydrogen can be generated from methanol through catalytic processes, using a fuel reformer [1-3].

Reformer is a chemical reactor designed for steam reforming of methanol. It has a packed bed of CuO/ZnO/Al$_2$O$_3$ catalyst inside an array of finned tubes. It receives feed from vaporizer in the form of superheated vapors and converts methanol into hydrogen by the steam reforming reaction. The main reactions that take place inside the steam reformer are: (a) Steam reforming of methanol, (b) Methanol decomposition and (c) Water gas shift reaction. Out of these three, the steam reforming and decomposition reaction are endothermic. The heat for these reactions is provided by the hot gases generated in the combuster. The hot gases flow over an array of reformer reactor tubes. These tubes are filled with packed bed of reforming catalyst. Being an exothermic reaction, the water gas shift reaction provides additional heat required to the endothermic reactions. Fig.1 shows the different streams in a methanol reformer-based fuel cell system. The methanol/water mixture is converted into hydrogen rich reformate gas by catalytic reactions. The endothermic reforming reaction takes place in a temperature range of 473 K to 573 K on copper/zinc catalyst [3]. The heat for these reactions is supplied to the tubular reforming reactor through the walls heated with hot gas or liquid.

Fig. 1.Methanol reformer-based fuel cell system.

For use of methanol as a hydrogen carrier for smaller capacity (sub 10 kW) fuel cell systems, the conventional steam reforming process must be scaled down. The integration of reformer and fuel cell requires effective heat integration within the system to achieve a better overall efficiency of fuel to electricity conversion [3-5].

Combining steam reformer (methanol steam reformer) with fuel cell (HT-PEM fuel cell) is an efficient method of generating electrical energy. Recycling the anode exhaust gas as fuel for generating heat for the reformer enhances overall efficiency of the system. Literature [6][7] reports the increase of > 30% in fuel utilization due to anode exhaust gas.

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The better overall efficiency can be achieved by incorporating the design of heat generation system based on catalytic combustion which can accept mix of fuel including methanol-water mixture, hydrogen rich reformate gas and the hydrogen lean anode exhaust gas. The combustor must handle all these types of fuel for efficient system operation and optimum fuel utilization during start-up as well as during normal operation.

Catalytic combustion, being a low temperature electro-chemical conversion process, is an alternative to conventional high temperature (>1273 K) flamed combustion and has substantial reduction in emissions. NOx emissions, a known dominant at higher temperature and being generally witnessed at conventional combustion mode, are lowered by incorporation of catalytic combustion. The catalytic combustion enables the reaction to take place at lower temperature due to the lower activation energy [8] and even a lean mixture of hydrogen (as in case of anode exhaust gas) can also undergo stable catalytic combustion [8-10].

The principle of catalytic combustion (conversion of chemical energy into thermal energy) process has matured from the fundamental work of Sir Humphrey Davy (1778-1829) [11][12]. Besides, the advantage of minimized emissions and the suitability towards fuel flexibility of handling multiple alternative fuels, the catalytic combustion also offer some other benefits such as - good temperature uniformity, robustness and simplicity in operation [8][13].

In general, catalytic combustion has been one of the well understood combustion techniques, but the effects of specific operating conditions such as variations in fuel compositions, flow rates, substrate type and catalyst loading, on performance of the catalytic combustor are not well understood. The catalytic reaction takes place on the active catalyst surface at temperatures below the ignition point of fuels such as methanol (737 K), hydrogen (773 K) and carbon monoxide (882 K).

The catalytic combustion with pre-mixed air-fuel gives lower emissions. Hence in this work the pre-mixing arrangement with provision for multiple fuel and air nozzles was chosen for investigation. This also brings in the advantage of having shorter length and time for mixing which also decreases possibilities of flashback and autoignition [8].

Based on available literature [9][14], the platinum on gamma alumina substrate is chosen as the combustion catalyst. Platinum has high activation energy which increases the rates of combustion reaction. This results in carrying out complete combustion of fuel at lower temperature [8][15].

II. CATALYTIC COMBUSTOR

It is a catalytic combustion based hot gas generator which is expected to have versatility of fuel from two/three different streams during start-up, stabilization and normal operation. The catalytic combustor performs a dual role in this process design. During start-up, it is expected to combust methanol water mixture form fuel tank followed by an additional incoming stream of early reformate. Once the reformate gas is supplied to fuel cell, the unreacted hydrogen, carbon monoxide and carbon dioxide from the anode exhaust stream is fed to the catalytic combustor as main fuel [16].

In catalytic combustor, there are three main combustion reactions and their reaction kinetics are considered - (a) methanol from methanol water mixture (b) hydrogen and (c) carbon monoxide at different compositions from reformate gas and anode exhaust gas. The basic reactions are [16-18]:

\[
\text{Methanol: } 2\text{CH}_2\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 4\text{H}_2\text{O} \tag{1}
\]

\[
\text{Hydrogen: } 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \tag{2}
\]

\[
\text{Carbon monoxide: } 2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2 \tag{3}
\]

Optimum air to fuel ratio is calculated by balancing the combustion reaction equation for the fuel. A stoichiometric mixture contains the exact amount of fuel and oxygen such that after combustion, all the fuel and oxidizer are consumed to form products. This ideal mixture approximately yields the maximum flame temperature, as all the energy released from combustion is used to heat the products [18]. The excess air stoic must be maintained across the combustor in order to avoid the temperature of the catalytic bed shooting over the required hot gas temperature of 623 K at outlet of combustor and to avoid catalyst deactivation. This excess air stoic is defined in equations (4) and (5) [6]:

\[
\lambda = \frac{(A/F)_{\text{real}}}{(A/F)_{\text{stoic}}} \tag{4}
\]

\[
\lambda = \left(\frac{A}{F}\right)_{\text{stoic}} \tag{5}
\]

In the design generally the approach is towards minimizing the transport limitations and maximizing the reaction rates (approaching the intrinsic reaction kinetics). The detailed numerical and empirical correlations are available from extensive experimental data for predicting the mass transfer effects and the different resistances to the reaction kinetics [9]. These effects are considered uniform across the catalyst bed for this investigation of the catalytic combustor design.

This paper reports the outcomes from design and experimental analysis of the catalytic combustor that provides heat at stable temperature to the methanol reformer. The catalytic combustor was modelled in EES and analyzed using all the three different types of fuel.

The experimental investigation was based on understanding operation and performance of the catalytic combustor, with respect to different operating fuels and their effects on the quality and quantity of heat generation for the reformer. The design was also subjected to a simulation using ANSYS DISCOVERY LIVE. It was also considered that for the lean-fuel mixture, the gaseous combustion reduction provides the rapid conversion and will not require a full simulation. Hence major side reactions can be neglected and homogeneous combustion, catalytic gas phase reactions are treated as single item for analysis [15]. The basic design includes a packed bed of combustion catalyst in 3 mm diameter cylindrical pellets of gamma alumina substrate coated with Platinum (0.3% Pt on γ Al₂O₃ structure). The combustor generated the hot gases at temperature below 623 K. These gases are used for supplying heat to methanol reformer and the feed vaporizer.
III. NUMERICAL MODELLING, SIMULATION & DESIGN

The EES model simulation was carried out considering fuel variations as per table 1. The same fuel configuration was used for experimental investigation.

Table-I: Fuels for experimental investigation

<table>
<thead>
<tr>
<th>Fuel Component</th>
<th>Methanol water mixture</th>
<th>Reformate gas</th>
<th>Anode exhaust gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃OH</td>
<td>56.0%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂O</td>
<td>44.0%</td>
<td>13.1%</td>
<td>14.0%</td>
</tr>
<tr>
<td>H₂</td>
<td>-</td>
<td>11.0%</td>
<td>3.2%</td>
</tr>
<tr>
<td>CO</td>
<td>-</td>
<td>1.5%</td>
<td>1.3%</td>
</tr>
<tr>
<td>CO₂</td>
<td>-</td>
<td>74.4%</td>
<td>81.5%</td>
</tr>
</tbody>
</table>

This fuel mix was arrived at based on the reformate gas composition through the methanol steam reformer [3] and then the possible gas composition at the HTPEM anode exhaust. The fuel gases were simulated for experimental investigation by using premixed gas cylinders with these known compositions. The combustion catalyst considered for this investigation is commercial catalyst of Pt - γAl₂O₃ (0.3% Pt) supplied by M/s. Dorf Kettle. The other catalyst properties considered for the model are as per table 2.

Table-II: Catalyst properties

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε</td>
<td>Catalyst bed porosity</td>
<td>-</td>
<td>0.35</td>
</tr>
<tr>
<td>ρₚₙₐᵣ</td>
<td>Bulk density of catalyst</td>
<td>kg m⁻³</td>
<td>735.0</td>
</tr>
<tr>
<td>Dₚ</td>
<td>Catalyst particle size in packed bed</td>
<td>m</td>
<td>3 × 10⁻³</td>
</tr>
<tr>
<td>Sₚ</td>
<td>Specific surface area per unit mass of catalyst</td>
<td>m⁻¹ kg⁻¹</td>
<td>210 × 10⁻³</td>
</tr>
</tbody>
</table>

The generalized combustion reaction equation can be written for the fuel combustion with air consisting of 21% O₂ and 79% N₂ [18].

\[ C_2H_5OH + (\alpha + \frac{3}{2} - \frac{3}{2})O_2 \rightarrow \alpha CO_2 + \frac{3}{2}H_2O + 3.76\left(\alpha + \frac{3}{2} - \frac{3}{2}\right)N_2 \] (6)

This equation (6) was solved for all the three fuels until optimal combustor outlet temperature was obtained with following assumptions and conditions [19]:

- The air fuel mix flow to the combustion combustor bed is an axial flow.
- Heat losses from the combustor are neglected.
- Air flow coming to the combustor is at constant pressure and ambient temperature.
- Only 3 key combustion reactions are considered, and all other reactions are neglected.
- At the inlet, the flow velocity, gas composition and temperature are kept constant and considered as user input.

The findings from the EES simulation on the catalytic combustion for all the three fuels generated guidelines for the experimental investigation as are shown in table 3.

Table-III: Fuels for experimental investigation

<table>
<thead>
<tr>
<th>Description</th>
<th>UoM</th>
<th>Methanol water mixture</th>
<th>Reformate gas</th>
<th>Anode exhaust gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower Heating Value of fuel</td>
<td>kJ kg⁻¹</td>
<td>11824</td>
<td>13452</td>
<td>4001</td>
</tr>
<tr>
<td>Stoichiometric O₂</td>
<td>kg per kg fuel</td>
<td>0.840</td>
<td>0.889</td>
<td>0.263</td>
</tr>
<tr>
<td>Possible flame temperature</td>
<td>K</td>
<td>1715</td>
<td>1865</td>
<td>1342</td>
</tr>
<tr>
<td>Required temperature</td>
<td>K</td>
<td>573</td>
<td>573</td>
<td>573</td>
</tr>
<tr>
<td>Excess stoic. required</td>
<td>-</td>
<td>7.40</td>
<td>8.38</td>
<td>7.08</td>
</tr>
<tr>
<td>Actual air flow required</td>
<td>kg per kg fuel</td>
<td>30.68</td>
<td>36.22</td>
<td>9.25</td>
</tr>
<tr>
<td>Lower Heating Value of fuel</td>
<td>kJ kg⁻¹</td>
<td>11824</td>
<td>13452</td>
<td>4001</td>
</tr>
</tbody>
</table>

IV. COMBUSTOR DESIGN

Design of catalytic combustor, as shown in fig. 2, is derived from the basic numerical analysis and is finalized for experimental investigation after subjecting through a CFD analysis using ANSYS DISCOVERY LIVE. The catalytic combustor was formed out of a cylindrical packed bed design. The experimental reactor contains a 50 mm diameter shell having a length of 100 mm for the mixing chamber to ensure proper air fuel mixture. It is followed by another 100 mm length filled with 145 gm of combustion catalyst (Dorf-Kettle) pellets and an exhaust chamber to allow withdrawal of the hot gases for further analysis. The packed bed of combustion catalyst was formed out of cylindrical pellets (each of 3 mm in diameter and 3 mm in height). The combustor design incorporates the air-fuel mixing arrangement formed out of air distribution plate having 8 outlets of 10 mm diameter for creating swirling action of air flow and radial fuel nozzles with 6 outlets of 2 mm diameter. The flow paths of air and fuel being perpendicular to each other assist the proper mixing of air and fuel.

The catalyst packed bed is required to be initially heated to achieve and maintain the catalyst bed in the active temperature region (> 373 K). Then the fuel is sprayed through the fuel nozzles. The swirl cum distributor plate installed at back of fuel nozzles, helps to generate the homogeneous air fuel mixture in the mixing chamber before it reaches the catalyst surface. This arrangement of air heater, air distribution plate, mixing chamber and then the catalyst bed forms the catalytic combustor design [20].
V. CFD SIMULATIONS

CFD simulations in the field of combustion are reported to be very complex. The grid generation and numerical solution to the equations can take substantial amount of time and computing power. The catalytic combustor design was also subject to a simple and quick CFD analysis using ANSYS DISCOVERY tool to derive meaningful conclusions and confirmation to validate the dimensional assumptions. By selecting the right boundary conditions, a CFD analysis became a valuable tool to model catalytic combustor configurations to get the proof on sub-models. This helped in comparing different configurations of air distributor plate, fuel nozzles and mixing chamber design. This quick analysis and ability to repeat and compare results within very short time helped in obtaining deeper understanding of the process. The CFD analysis results on finalized sub-system components of the catalytic combustor are given in fig. 3.

The pressure drop analysis enabled the design of experiment and contributed to derive the operating parameters for the experimental set-up.

VI. EXPERIMENT

The experimental set-up includes a combustion catalyst packed bed reactor, a mixing chamber, HPLC pump & electrical vaporizer for methanol water mixture fuel, gas cylinders with premixed gas composition of reformate gas and anode exhaust gas. An air heater is provided for initial heating of air and to initialize the catalyst bed activity during start of the experiment from ambient conditions. The fuel flows are monitored and controlled through Alicat mass flow controller for gases and through HPLC pump for methanol water mix. A Honeywell MultiTrend SX paperless data recorder is used for monitoring and recording all the operating parameters.

The combustion gas temperature is measured at outlet of catalyst bed. The flow of air supplied to the catalytic combustor was modulated and controlled in such a way that the combustor outlet temperature of hot gases is maintained at temperature above 573 K. Before start of the experiment, the catalyst bed was pre-heated to 373 K by controlled hot air flow, generated through electrical air heater. After achieving the temperature inside the catalyst bed, the bed was supplied with flow of all three fuels.

In the first experiment, the methanol water mixture was prepared with same steam to carbon - S/C ratio (1.4) as feed to the reformer. The methanol water mixture contained 60% methanol by volume. The fuel flow to catalytic combustor was supplied by the peristaltic HPLC pump through the electrically heated vaporizer to generate superheated vapors at temperatures above 393 K. This air-fuel mix flow resulted in gas hourly space velocity (GHSV) across the packed bed combustor of above 20000 h\(^{-1}\). The fuel was sprayed into the mixing chamber using radial nozzles drilled on a fuel supply tube. The combustion reaction was carried out, which resulted in generation of hot gases. The temperature was raised from 373 K to 573 K. After reaching 573 K, the hot gas temperature was maintained by modulating the air flow at inlet of catalytic combustor with maximum flow limit of 10 m\(^3\) h\(^{-1}\). The entire stream of the hot gas mixture coming out from combustor was cooled in a water-cooled heat exchanger (cooler) to separate out...
the condensable components. The non-condensable components coming out from the cooler were measured using gas flow meter. Gas samples were then collected in Tedler bags for analysis using gas chromatograph (Thermo-Scientific, TRACE 1110 with TCD and FID columns) for concentration of all the species (nitrogen, oxygen, methanol, water vapor, carbon dioxide, carbon monoxide and other pollutants such as NOX & SOX). Similar experiments were carried out with reformate gas and AEG as fuel. The experimental set-up schematic is as shown in fig. 5 below.

![Fig. 5. Experimental assembly.](image)

**VII. PERFORMANCE**

The performance of the catalytic combustor, comprising of complete combustion of fuel and time to achieve the required hot gas temperature at outlet, was measured at various conditions. Fig. 6 shows the temperature variation of the catalytic combustor as a function of the reaction time. This plot includes the temperature variations at combustor outlet. During testing at a fuel feed rate of 3.5 ml min\(^{-1}\) (187 gm h\(^{-1}\)), the temperature of the catalytic combustor reached 473 K within 21 minutes after initiation of the combustion reaction (test 1 data in fig. 6). The fuel feed rate, air flow rate along with operating conditions were modulated to reduce the time for the start-up.

At a feed rate of 4.0 ml min\(^{-1}\) (214 gm h\(^{-1}\)), the combustor temperature reached 473 K within 15 minutes after the start of operation (test 2 data in fig. 6). It was observed that, as the fuel rate increased, the time for the start-up decreased. Similar trends were observed in test 3, 4 and 5 (shown in fig. 6). However, the combustion reaction residence time (which is inversely proportional to fuel feed rate) got reduced. Furthermore, it also increased probability of generation of hotspots in the foremost part of catalyst bed, which is expected to cause increased catalyst deterioration/decomposition.

![Fig. 6. Combustor tests - Temperature profiles.](image)

To validate the design and operational performance of catalytic combustor; the EES simulation results were compared with experimental data. The experimental results are reported with respect to the complete combustion of methanol water mixture, reformate gas and AEG. The gas analysis results obtained from gas chromatography during the different experiments are shown in tables IV, V and VI along with fig. 7, 8 and 9. It was also observed that, there were no traces of unreacted fuel, CO, NOX, SOX or any particulate matter found in the combustor outlet gas.

These experiments were conducted with the guidelines derived from EES simulations. The fuel flow is arrived based on lower heating value (LHV) of fuels for to generate the necessary quantity of heat as required by the reactions of methanol reformer [3].
The excess air flow was maintained across the combustor to avoid a temperature overshoot beyond 623 K as the temperature beyond 623 K would cause irreversible damage to the reforming catalyst. This resulted in air stoichiometry of 7.4 in the air-fuel mix at combustor inlet. The achieved combustor outlet gas composition was then compared with simulation results. It was found that the simulation results
and experimental investigation were in agreement for all three fuels. The fuel combustion in catalytic combustor is mainly dependent on the proper air fuel mix and the operating parameters.

VIII. CONCLUSION

A new catalytic combustor concept has been developed, tested and validated for the methanol reformer. The new catalytic combustor system consists of an air distributor plate, fuel nozzles, mixing chamber and combustion chamber filled with packed bed of combustion catalyst. This catalytic combustor design was based on a steady-state analysis for combustion reaction kinetics and thermal management for providing heat for on-board methanol reformer. The design was discussed with packed bed configuration of Pt-γAl2O3 catalyst. The guidelines for the experiments were arrived based on the EES simulations. The experimental investigation was found in strong agreement the EES simulations. An analysis was done on the different fuels during normal operation of experimental methanol reformer. This investigation enabled the basic guidelines for design of catalytic combustor for on-board methanol reformer for 5 kW HT-PEMFC application. The final configuration of catalytic combustor will have a 105 mm diameter packed bed reactor with 225 mm bed length and equivalent length of mixing chamber before the catalyst bed. This has similar design configuration as that used in this experimental investigation. This guideline of combustor was estimated from minimum hydrogen flow required for the HT-PEMFC operation [3] [20].

In experimental investigation, it was observed that combustor exhaust emissions are very low (THC, CO and NOx are at nearly zero level). Thermal efficiency for hydrogen generation is higher than 80% [3]. It also achieves in a very important objective of high degree of thermal integration for efficient system operation. Recent literature also reports the sensitivity of elevated operating temperatures on reformate gas composition which will affect the fuel cell. Hence it is critical to have a controlled catalytic combustor design integrated with on-board methanol reformer for HTPEM fuel cell. This also needs further investigation towards improving the reliability of integrated methanol reformer for at least several thousand hours of operation. It should also have minimum thermal distortions during normal operation, more compactness of the system, higher efficiency and faster response.

REFERENCES


AUTHORS PROFILE

Abhijet Chougule, received B.E. (Power Engineering) from National Power Training Institute (NPTI) Nagpur through Rashtrasant Tukadoji Maharaj Nagpur University (RTMNU) in 2007 with Gold medal. Currently he is pursuing his integrated MTech-PhD studies from the Department of Technology, Savitribai Phule Pune University, India. Since 2007, he has also been working as Scientist at Research, Technology & Innovation Center of M/s. Thermax Ltd. Pune, India. His areas of interests are Fuel reforming, hydrogen generation and Fuel cells.

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