Influence of Different Hydrogen/Methane Mixtures on the Operability of Small-size Burners for Energy Production

A. Morandi¹, G. Zizak², F. Cignoli², M. Derudi¹

1. Politecnico di Milano - Dip. di Chimica, Materiali e Ingegneria Chimica “G. Natta”/CIIRCO, Milano - ITALY
2. CNR-IENI, Istituto per l’Energetica e le Interfasi, Milano – ITALY

1. INTRODUCTION
In the last decades a big interest in process intensification and in reactor and equipment miniaturization has grown up. Efforts have been made in order to manage traditional processes in small size systems to make this processes more flexible and safe. Examples of these processes like steam reforming of methanol or synthesis of dangerous substances can be easily found in the literature [1-2]. Nevertheless the more interesting application of these micro-systems is the power generation. The dramatic increase in the number of electronic devices drives to look for a more efficient solution than the traditional electro-chemical batteries. The idea is to use the high energy density of hydrocarbons to produce electrical power [3]. For this reason, an experimental study has been performed to develop and characterize a device which is able to convert the thermal energy released during the combustion in electric power by means of thermo-electric modules.

As highlighted in a previous work [4], the behaviour of the system is mainly conditioned by: 1) catalytic bed, necessary to support the combustion, 2) thermal conductivity which is important to provide a good wall temperature for the thermo-electric modules, 3) design of the combustion chamber and 4) feed range. Additional information about these factor will be given in the experimental results section.

In particular, this work demonstrates the functionality of the devices and produces interesting performance in terms of combustion sustainability using stoichiometric mixture of H₂/Air and H₂/CH₄/Air in a wide range of flow rates.

2. EXPERIMENTAL SECTION
In this work two different burners were studied. The second burner was developed in order to improve the performances and solve the problems of combustion sustainability found with the first burner using the H₂/CH₄/Air mixture.

Both the burners use a catalytic packed bed built with cylindrical pellets constituted by 1% of Pt supported on Al₂O₃. The burners dimensions are due to the dimensions of the thermoelectric modules, which have a square section with a side of 30 mm.

The first micro-burner, reported in figure 1a, has a rectangular shape and it is constituted by an aluminium support to which are fixed the feeding brass pipe and two copper plates. The copper plates have the function of limiting the combustion chamber and to provide an hot surface for the thermoelectric modules. For this reason the material has a good thermal conductivity in order to ensure high and uniform temperatures at the modules. As shown in figure 1a the combustion chamber is funnel-shaped to avoid stagnation regions. This chamber is filled with 65 catalytic pellets, randomly packed. The simplified design of this burner give it little thermal inertia, easiness of use and maintenance. The small dimensions of the metal supports allow to reach steady-state conditions in 20-25 min. The high thermal conductivity
has a double function: sustain the combustion and provide a high and uniform wall temperature. On the other hand this high conductivity produces high external heat losses. A catalytic system is needed because of these losses. Finally the easy configuration of the packed bed allows for studying the influence of the catalyst load and its position within the combustion chamber.

The negative aspects of the rectangular burner are the absence of an adequate pre-heating of the reactants, an insufficient heat recovery (the combustion gases leave the system at high temperature) and a fixed orientation of the burners, to avoid the loss of catalytic pellets. The burner position is important during the start up, when the combustion chamber is cold. In these conditions the water produced by the combustion condenses and accumulates in the bed. Moreover the poor heat recovery is a penalization of the global efficiency of the systems, while the insufficient pre-heating of the reactants gives some problems with the methane combustion. The methane ignition need a bed temperature higher than that for hydrogen. For this reason in the rectangular burner CH$_4$ is ignited only in the presence of high H$_2$ streams. After the ignition of methane, hydrogen is still needed to sustain the combustion reaction.

Since it was found that the rectangular burner cannot be operated with CH$_4$, a second burner was developed in order to improve system capabilities and to enlarge the stability limits of the combustion.

The absence of a good pre-heating of the feed was identified as the more critical aspect. So the second burner, shown in figure 1b, has two twin chambers separated by a bronze porous plate. The lower chamber of figure 1b is the pre-heating chamber. The fresh reactants enter in the pre-heating chamber filling it. Reached a fixed pressure, imposed by the porous plate pressure drops, the reactants enter into the combustion chamber, filled with 145 catalytic pellets, where they burn. The heat generated by the reaction increases the temperature of the whole system. By this way the reactants enter the combustion chamber with an higher temperature and a slower velocity that in the rectangular burner. The closed combustion chamber allows to dispose the burner with the gas outlet directed towards the ground to evacuate easily the liquid water produced during the initial stage of the experimental run.

This new burner, the cylindrical one, presents a bigger thermal inertia, due to the larger metal supports that increase the time needed to reach steady-state conditions to 30-35 minutes. Although this burner demonstrates good performances with hydrogen and methane too. In fact the methane can be ignited with little fraction of Hydrogen and once reached steady-state conditions it is possible to turn off the hydrogen feed without the burner shut down.

![Design of the two burners with their characteristic dimensions.](image)
3. RESULTS AND DISCUSSION

First of all a characterization of the combustion performances was made to determine both the wall and the gas temperatures varying the feed composition. Then, other experiments were done to verify the effective power generation of these burners. The electrical power depends strongly on the temperatures at the two sides of the thermoelectric modules. In fact the power generation is proportional, by means of the Seebeck’s coefficients, to the temperature difference between the hot, near the combustion chamber, and the cold side of the thermoelectric modules. Before reporting the value of power generation some considerations about the combustion sustainability will be given.

With the rectangular burner a set of preliminary tests were made to verify the influence of the catalyst load and the role of its position within the burner.

The first experiment was made in absence of active phase. The combustion chamber was filled with pellets of Al₂O₃ without the catalyst, Pt. In this configuration even the hydrogen, which is more reactive than methane, did not react, confirming the necessity of the catalyst. Afterwards to investigate the influence of the catalytic load a set of experiments with three different bed configurations was carried out. In particular the configurations with 6, 12 and 24 catalytic pellets were selected. In order to keep unchanged the bed property, the rest of the combustion chamber was filled with inert pellets. Figure 2a shows the trend of the exhausts temperatures for the three configurations as a function of the Hydrogen fed.

Figure 2: Exhausts temperatures versus the hydrogen flow-rate: (a) catalyst load influence, (b) catalyst position influence.

The temperatures of the exhaust gases increase linearly with the increase of the H₂ stream, in fact the R² factor is close to the unity. Figure 2a also shows a small influence of the catalyst load. The combustion of Hydrogen is complete with only 6 active pellets. A bigger catalyst load does not improve the system performances. The small temperature difference found for the three configurations is probably due to a different thermal behaviour of the packed bed during the heat-up phase. However for the following experiments a configuration with a bed fully constituted by catalytic pellets has been chosen in order to avoid loss of reactants especially with methane.

Figure 2b shows the results of the experiments done to study the influence of the catalyst position. Also in this case there no large differences have been found among the various configurations. The temperatures of the exhausts measured with the configuration in which the catalyst was located in the intermediated region of the chamber are a little bit higher than the temperatures obtained with the catalyst set at the beginning of the chamber. This fact is probably due to the short length of the bed after the reaction zone. If the combustion takes place in the intermediated region of the bed, the hot gases have to heat up a little portion of bed after the reaction so they leave the burner with higher temperatures. The configuration
with the catalyst in the intermediated region of the chamber was realized by using inert pellets in the rest of the chamber in order to keep constant the total number of pellets in all the experiments. After this preliminary characterization a set of experiments were made to evaluate the burner performance with a hydrogen fee, then with a H₂/CH₄ mixture in stoichiometric condition. The hydrogen flow-rate has been varied from 0.09 Nl/min up to 0.3 Nl/min obtaining wall temperature at the steady state between 90 and 180°C. The linear trend of the temperatures, increasing the hydrogen flow rate, is an evidence of the complete fuel conversion. Using methane, the first burner showed a strong difficulty to activate the combustion reaction. The CH₄ addition did not produce an increase of temperature. Besides the failed activation of the methane combustion it was found a partial deactivation of the catalyst that increase the ignition difficulty. The hydrogen co-feeding was necessary also after the burner start up to avoid the reaction to be switched off. These negative aspects highlighted with the first burner were the input for the construction of the twin-cylindrical burner. Because of the design of the combustion chamber, in this case, the evaluation of the influence of the catalyst was skipped. The reactants are well mixed and spread over the whole section, so it is necessary a complete coverage. For this reason the bed was fully active to avoid leak of reactants. Also for the cylindrical burner the characterization started using only hydrogen and in a second time methane has been added. Figure 3 shows the temporal evolution of the wall temperatures varying the hydrogen flow-rate of the feed.

Figure 3: Temporal evolution of the wall temperatures varying the hydrogen flow-rate with the cylindrical burner.

Increasing the hydrogen amount fed to the burner the wall temperature in steady state conditions are increased too. Also the initial step of temperature is bigger for the higher flow-rates; anyway, the time needed to reach steady-state conditions remains constant at 30-35 minutes. Reporting the final temperature of these curves, versus the hydrogen amount, in a diagram all the data show again a linear trend. Once verified the good functionality of the system over a wide range of hydrogen flow-rates, experiments with a hydrogen/methane mixture were performed using a two-step procedure and a single step procedure. With the two-step procedure methane was added after reaching steady-state conditions with the hydrogen combustion. First of all it was determined the smallest hydrogen flow-rate necessary to ignite the methane combustion. Using the two-step procedure a flow-rate of 0.057 Nl/min was found while with the single-step procedure is 0.115 Nl/min of H₂ are needed. This difference is due to the bed temperature. For the single step procedure an higher hydrogen amount is needed to heat more
rapidly the bed, otherwise the bed temperature is too low for ensuring the methane ignition and the system loose activity. For this reason to avoid deactivation problems with the catalysts, next tests were performed with the two-step procedures.

![Figure 4](image_url)

**Figure 4:** (a) wall temperature varying methane and hydrogen flow-rates, (b) comparison between the inner temperatures and the wall temperatures for different mixture composition.

Figure 4a shows the wall temperatures versus the H$_2$/CH$_4$ composition of the fuel mixtures, respectively with 0.115, 0.230 and 0.345 NL/min of H$_2$ as base-constituent of the mixture. The diagram shows again a linear trend between wall temperatures and the alimentation streams. It also shows that the curves tend to converge for the higher flow-rates. This phenomenon is due to the larger heat losses and the higher velocity of the gases, that reduce the time to realize an effective heat exchange at the walls. The figure 4a displays a maximum wall temperature of 250°C, but the thermoelectric modules have a limit temperature of 200°C. Then a good choice of the feed stream is fundamental.

To have a better description of the system, experiments to measure the inner temperatures were also made. In order to maintain the thermocouple in the right position an aluminium holder was added to the burner. This device increases the external heat losses so for the same flow-rates smaller wall temperatures were reached than the previous attempts.

Figure 4b shows a comparison between the inner temperature and the wall temperature for different H$_2$/CH$_4$ mixtures. It is possible to notice that a flow-rate increase induces an increase in the $T$ between walls and bulk of the burner; this confirms the previous assumptions concerning a loss of efficiency in the heat exchange due to a reduction of the gas residence time within the burner. This configuration gave the possibility to evaluate the ignition temperature for the methane, which is near the 100°C. From this information it is possible to determine the best start up strategy. This strategy consists on feeding a high hydrogen flow-rate until 100°C are reached then introducing immediately the methane while turning down the hydrogen feed in order to avoid possible damages to the thermoelectric. This strategy allows for reaching a wall temperature near 200°C, the best temperature for the thermoelectrics modules, in a short time.

Once it was verified the possibility to sustain the combustion in a wide range of flow-rates and mixtures compositions, power generation measurements were performed. For these experiments the burner was equipped with the two thermoelectrics modules and two water-coolers, as shown in figure 5. The coolers have the function to maintain the cold side of the thermoelectrics under 50°C, recovering at the same time part of the heat producing hot water. However, this new configuration introduces other external heat losses that limit the burner
temperature. Besides the cold and the hot side are not perfectly independent. This means that the temperature difference across the thermoelectrics modules is a bit penalized. In table 1 are reported the measurements of power generation. When the temperature difference between hot and cold sides increases also the voltage and the electrical intensity increase. Table 1 reports the value of power generation and an estimated energy conversion efficiency. This efficiency is valued comparing the electric power produced with the thermal power supplied by the fuel. In the best condition the cylindrical burner reach an efficiency of 1.3% that is a quite good result if compared with other literature studies [3, 5].

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.345</td>
<td>0</td>
<td>101</td>
<td>28</td>
<td>3.28</td>
<td>150</td>
<td>56.5</td>
<td>0.49</td>
<td>0.87</td>
</tr>
<tr>
<td>0.46</td>
<td>0.038</td>
<td>160</td>
<td>37</td>
<td>5.44</td>
<td>204</td>
<td>96.2</td>
<td>1.11</td>
<td>1.15</td>
</tr>
<tr>
<td>0.46</td>
<td>0.077</td>
<td>175</td>
<td>30</td>
<td>6.46</td>
<td>224</td>
<td>117.1</td>
<td>1.45</td>
<td>1.24</td>
</tr>
<tr>
<td>0.46</td>
<td>0.115</td>
<td>195</td>
<td>30</td>
<td>7.31</td>
<td>234</td>
<td>138</td>
<td>1.71</td>
<td>1.24</td>
</tr>
<tr>
<td>0.57</td>
<td>0</td>
<td>142</td>
<td>27</td>
<td>5.15</td>
<td>198</td>
<td>94.1</td>
<td>1.02</td>
<td>1.08</td>
</tr>
<tr>
<td>0.57</td>
<td>0.038</td>
<td>174</td>
<td>28</td>
<td>6.37</td>
<td>222</td>
<td>115</td>
<td>1.41</td>
<td>1.23</td>
</tr>
<tr>
<td>0.57</td>
<td>0.077</td>
<td>198</td>
<td>27</td>
<td>7.3</td>
<td>240</td>
<td>136</td>
<td>1.75</td>
<td>1.29</td>
</tr>
</tbody>
</table>

Table 1: Power generation for different feeding conditions.

Figure 5: Burner with thermoelectric modules and water-coolers.

4. REFERENCES