ABSTRACT:
This paper presents a reformer prototype for the production of the necessary H2 to supply a 5 kW PEMFC and its first results. The fuel processor consists of an OSR and a WGS and a PROX reactors. The design of the system was carried out with a one-dimensional model [1,2]. The mixture chamber was specially studied with a CFD code (Fluent®), taking into account the effect of fuel evaporation and the cool flame process. The aim of the designed facility is to be able of characterising each component and controlling each working parameter. Eventually, using diesel as fuel, results from the mixture chamber, OSR, WGS and PROX reactors are presented. It also includes conclusions and future works.

KEYWORDS: Reformer, Fuel Processor, diesel fuel

1. INTRODUCTION
Nowadays, there is a growing interest in hydrogen technologies. This happens because fuel cell is one of the most promising technologies for electric generation, being one of its most outstanding characteristics its high efficiency. In this way, by means of a purely electrochemical process, fuel cell converts directly chemical energy of the fuel into electric energy.

The fuel mostly used in fuel cells is hydrogen, but also methanol or natural gas can be used depending on the selected fuel cell. Hydrogen in one of the most abundant elements on earth, but its main drawback is that it is always found combined forming water, hydrocarbons,… Fossil fuel is a very important source for hydrogen generation by means of reforming processes. Reforming processes consists of the chemical transformation of fossil fuels by means of catalysts included in different reactors [3-4] to produce hydrogen. In fact, it is the most currently used method for hydrogen production and it will continue being up to the moment in which hydrogen production by means of cleaner sources could be available, such as water electrolysis using renewable energies. Gaseous fuels (natural gas) will be more useful for generating hydrogen in large-scale or in residential sector, whereas reforming processes from liquid fuels (gasoline, diesel fuel, methanol,…) will be more used in vehicles (on-board reforming) or for small energy generators in isolated zones. Using liquid fuels for hydrogen production implies lower performances in the whole process (regarding gaseous fuels), but they have the advantage of a higher energetic density, which favours storage in reduced volumes and they also have a distribution infrastructure all over the world.

This paper is placed in this context, being a result of the project “Development and construction of a 5 kW diesel fuel reformer”, jointly developed by INTA, ICP-CSIC, AICIA (Association of Research and Industrial Cooperation of Andalucia) and CIDAUT.

This project started about the middle of 2003 with the aim of developing an alternative energy generation system to combustion engines, using the same fuel. Nowadays, the first stage of prototype development that is able to control each working condition of the components (reformer and fuel cell) has been accomplished. In the following years the target is the development of a new mock-up in which necessary improvements regarding thermal integration, autonomy, sizing reduction, starting time and performance will be added, so that it could be competitive in performance compared with combustion engines.

1.1. Description of the reactors.
The main reactor is where the reforming reaction takes place. There are three different types of reforming processes depending on the reaction that happens. They are collected in Table 1.
Table 1. Summary of the three more used reforming processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Equation</th>
<th>( \Delta H^\circ ) (kJ/mol)</th>
<th>Reaction temperature (°C)</th>
<th>% Yielded Hydrogen</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam Reformer (SR)</td>
<td>( \text{C}_n\text{H}_m + 2n \text{H}_2\text{O} \rightleftharpoons n \text{CO}_2 + (2n + m) \text{H}_2 )</td>
<td>1280</td>
<td>750</td>
<td>55</td>
<td>Slow start-up, External heating system</td>
</tr>
<tr>
<td>Partial Oxidation Reforming (POX)</td>
<td>( \text{C}_n\text{H}_m + \frac{n}{2} (\text{O}_2 + 3.76\text{N}_2) \rightleftharpoons n \text{CO} + m \text{H}_2 + \frac{n}{2}·3.76 \text{N}_2 )</td>
<td>-659</td>
<td>1100</td>
<td>28</td>
<td>Quick and easy start-up</td>
</tr>
<tr>
<td>Oxidative Steam Reformer (OSR)</td>
<td>( \text{C}_n\text{H}_m + a\cdot n (\text{O}_2 + 3.76\text{N}_2) + b \cdot n \text{H}_2\text{O} \rightleftharpoons p \text{CO} + q \text{CO}_2 + r \text{H}_2 + s \text{H}_2\text{O} + a\cdot n·3.76 \text{N}_2 )</td>
<td>0</td>
<td>850 - 900</td>
<td>35-40</td>
<td></td>
</tr>
</tbody>
</table>

More detailed information about each reaction is available in [5]. In the Oxidative Steam Reforming the pretended aim is achieving a null global energetic balance. In this type, as reactors, steam and air are used. \( O_2/C \) and \( H_2O/C \) ratios for diesel fuel, depending on different authors, [6-9] varies from 0.3 to 0.5 and 2 to 3 respectively. The two reactions do not take place uniformly throughout the reactor, but in the first zone is where partial oxidation takes place (along few centimetres). It is also where the main percentage of the \( O_2 \) introduced is consumed and where the heat for the rest of the reactor is supposedly produced. In the rest of the reactor and thanks to the heat provided and to the presence of steam the endothermic reaction is produced. In fact, it is always necessary to provide extra heat to the medium and lower part of the reactor.

In this project, the third design was chosen, due to participate of the advantages of both methods, and because it is the tendency of most of the researchers when liquid hydrocarbons with low H/C ratio, as for example the diesel fuel, are considered.

A Water Gas Shift (WGS) Reactor for CO elimination and hydrogen enrichment of the gas mixture follows. Before the input of the fuel into the WGS is convenient to carry out a desulphurisation in order to avoid catalytic poisoning. More information about this reactors can be found in [10-12]. There are two types of WGS reactors: High Temperature WGS (HTWGS) and Low Temperature WGS (LTWGS). In both the reaction that takes place is:

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2
\]

In this reactor not only CO is eliminated but \( H_2 \) quantity is increased, so in fuels with low H/C ratios is very advisable its use. In this particular case a LTWGS was set at the output of the OSR because CO concentration inside the reforming gas is less than 8%.

For reducing the percentage of CO down to the value required by the PEMFC manufacturer, it is necessary to include another purification stage in which the CO is eliminated by means of oxidation in a Preferential Oxidation Reactor (PROX Reactor), described in [13]. The reaction that happens inside this reactor is:

\[
\text{CO} + 1.5 \text{H}_2 + (0.5+0.75) \text{O}_2 \rightleftharpoons 1.5 \text{H}_2\text{O} + \text{CO}_2
\]

This process involves a catalyst of which its selectivity involves the removal of 1.5 mol of \( H_2 \) for 1 mol of CO removed. This fact is not very important due to the low percentages of CO in the stream.

2. EXPERIMENTAL

In this section, the experimental apparatus and the operating process of the diesel reformer are briefly described. Previously to the description it could be remarked that the developed facility could be considered not only as an integrated reformer, but also as a facility that allows testing and characterising the different components of the reformer (reactors, heat exchangers) in an isolated and coupled way under different working conditions. The objective has not been yet the full thermal integration of the components.

2.1. Facility description

The reformer design was carried out considering that it has to be able of supply enough hydrogen flow-rate to make work a 5 kW Proton Exchange Membrane Fuel Cell (PEMFC). So, and considering the data given by the fuel cell manufacturer, the flow rate was fixed supposing a stack performance of 40% and an excess of hydrogen of 1.55 in the supply current. With these values, and taking into account the data fed by the ICP-CSIC regarding \( O_2/C \) and \( H_2O/C \) ratios (between 0.3-0.8 and 2-5 respectively), the maximum flow rates for reactors and the products to be supplied were fixed. For diesel, with \( O_2/C \) ratios of 0.5 and \( H_2/C \) of 3, the maximum flow rates were 2.64 l/h for diesel fuel, 8.44 Nm³/h for air and 11.44 Nm³/h for steam.

The reformer consists mainly of 3 reactors, OSR, WGS Reactor and PROX Reactor, which contain volumes of 2.61, 3.16 and 11.25 l respectively, and they possess a spatial velocity at maximum flow rate and in optimal working conditions with diesel fuel of 12710, 14230 and 2850 h⁻¹ respectively. These reactors have
an electrical heating system that allows them to achieve the necessary temperatures for each working stage of the reformer. The WGS and PROX Reactors can even be cooled as a function of the heat released during its reaction.

The sizing of the facility was carried out by means of a one-dimensional model, described in [1-2], that allows the simulation of not only the behaviour of the reactors (using thermodynamic and chemical kinetic reactions) but also the heat exchangers (with heat transfer equations). As results of the simulation temperatures evolution throughout the facility and sizing of the components were obtained.

In Fig 1, the operational diagram of the facility, below described, is presented. The reformer has 5 input lines: Steam, air, diesel fuel, nitrogen and hydrogen. The first three are used during the normal working of the reformer and the other two only during the starting up. Nitrogen and hydrogen share input line with air because they are never going to be used simultaneously with it. The air and steam are mixed and heated in an electrical heater up to 320ºC approximately. In the mixing chamber the mixture of the gas from the heater with the diesel fuel is accomplished by means of the cool flame process. This mixture is then introduced into the rest of reactors included in the facility: OSR, Desulphuriser, WGS and PROX Reactors. Between the different reactors there are heat exchangers (HE) that permit to adapt the input temperature at each reactor to the design temperature.

A system for gas analysis allows the measurement of the gas composition at different points in the facility. This system has two cooling units to cool the water flow used to reduce reforming gas temperatures in the heat exchangers, condensers and WGS and PROX Reactors. In the Fig 2, a couple of photographs of the test facility are presented.

In each reactor, 6 thermocouples at different heights are inserted, in a normal way to the flow in the OSR, or longitudinally in the Desulphuriser, WGS and PROX Reactors. From the recorded data, it is possible to obtain the temperature profile in each reactor. In the OSR each thermocouple controls a block of
resistances, so there are 6 heating blocks. However, in the rest of reactors only one thermocouple controls the whole heating system, although it can change as a function of the gas flow that goes through the reactor.

The sequence of global starting up is carried out in several steps. First of all, there is a heating stage for removing any water retained (due to previous experiment) from the catalyst. This is accomplished by heating the heater, mixing chamber, OSR, Desulphuriser, WGS and PROX Reactors with a high flow rate of air up to a temperature between 150 and 200ºC. Afterwards reactors catalysts are reduced with H₂ for ensuring that they are activated. The reduction is achieved with a mixture of nitrogen and 10% of hydrogen. Reduction temperatures are: 350ºC for the OSR, 250ºC for the WGS and 200ºC for the PROX Reactor. After that, each reactor is heated up to the process temperatures. 320ºC for the heater, 480ºC for the mixing chamber, 800ºC for the first block of resistances of the OSR and 900ºC for the rest, 450ºC for the Desulphuriser, 290ºC for the WGS and 170ºC for the PROX Reactor.

3. RESULTS
A test planning was prepared to characterise the behaviour of the electric heater, mixing chamber and OSR reactor at different flows. Decaline and diesel fuel were used as fuels and different tests were carried out in the ICP-CSIC laboratory, in a laboratory microreactor described in [14], and in CIDAUT described in [15], in the reformer installation described in this paper.

The microreactor characterisation consisted of adjusting the heating PID parameters and tests at different process temperatures. The characterisation and validation of the mixing chamber and OSR are described in the following sections.

3.1. Mixing chamber characterisation
Simulations of the fuel vaporisation that takes place in the mixing chamber were carried out, as those showed in the Fig 3 (described in [16]), where the process of diesel fuel drops vaporisation is shown at different moments along its advance through the mixing chamber. Different tests were also carried out in-situ for studying the mixing process suitability; testing different diesel fuel feed systems and different process temperatures. The cool flame process was also studied.

The mixture formation constitutes a clue factor in the quality of the following stage of reforming because mixture homogenisation prevents the appearance of hot spots and coking. The cool flame makes possible to evaporate the liquid hydrocarbons free of residues. Cool flames started when a liquid hydrocarbon is vaporised in a preheated air current [8,17]. These reactions, for the diesel fuel case, begin to happen at a temperature of 300ºC, stabilising at temperatures close to 480ºC.
Cool flames allow also to achieve a stable temperature, which helps very much in the mixing and homogenisation process because in the reactions, slightly exothermic, that take place during its development the heaviest diesel fuel fractions of the hydrocarbons chains are broken, aiding to the posterior process of reforming.

3.2. OSR validation with diesel fuel
A test plan for characterising the OSR reactor with a low-content sulphur diesel fuel (less than 50 ppm of sulphur) has been designed by ICP-CSIC and CIDAUT. In this way, in the ICP-CSIC facility necessary tests for characterising the new catalysts and defining working conditions were carried out. Afterwards, the catalyst was tested in the OSR reactor in CIDAUT presented in this paper. In CIDAUT reactor was filled, as happened in the Ni catalyst, half the volume with catalyst and the other half with inert. All the tests were accomplished with cool flame.

Firstly, it was obtained that the ideal reforming temperature for diesel fuel was 850ºC. Then tests presented in Fig 4 and 5 were carried out. In these graphs H₂ variations versus O₂/C and H₂O/C ratios are shown. Tests were carried out in the ICP-CSIC facilities. From these graphs, it was taken the decision that the optimum O₂/C ratio was 0.5 because with it acceptable values of H₂ concentration throughout time were obtained and, moreover because the amount of inert gases introduced was not very high. The selected value of H₂O/C ratio was 3, because it was the minimum value for which the concentration of produced H₂ remained stable during the process.

![Graph of H₂ concentration](image1.png)

**Fig 4.** Time evolution of H₂ concentration for different values of H₂O/C ratio. It was accomplished in ICP-CSIC facilities. Reforming temperature of 850ºC

![Graph of H₂ concentration](image2.png)

**Fig 5.** Time evolution of H₂ concentration for different values of O₂/C ratio. It was accomplished in ICP-CSIC facilities. Reforming temperature of 850ºC

Once obtained the optimum values of O₂/C and H₂O/C ratios, tests were carried out in CIDAUT. Results concerning concentrations are collected in Fig 6. In both, it can be clearly observed how when O₂/C ratio increases N₂ and CO₂ concentrations increase and H₂ and CO concentrations decrease. In this case, the expected tendency regarding CO₂ increase with O₂/C ratio increase is fulfilled. This was because, in this case, OSR resistances worked at maximum power with the aim of maintaining the reactor as much adiabatic as possible. The reformer performance increases with the decreasing of the O₂/C ratio due to the increase of H₂ concentration at the inlet.

In this case, as well as in the decaline case, outlet gas composition hardly change with an increase of the H₂O/C ratios, so most of the tests were carried out with the minimum possible ratio (although always higher than 3). This agrees with the results form the small-scale tests accomplished in ICP-CSIC facilities and by other authors [7,9].
Fig 6. Outlet gas composition versus O₂/C ratio. Reforming temperature 850°C and diesel flow rate 1 l/h. H₂O/C rate was between 3 and 3.5.

A comparison between results presented in this paper for diesel fuel and results obtained by other authors, that use a fuel that simulate the diesel composition, [7,9] are presented in Fig 7. It is clear that results presented in this paper have similar tendencies.

Fig 7. Outlet gas composition versus O₂/C ratio. Reforming temperature 850°C. H₂O/C rate was between 2 and 3.5. In black are results from this facility and in grey and white the results shown by [7] and [9].

Fig 8. Reformer gas composition and temperature profile at different points of the facility: (a) output of WGS Reactor and (b) output of PROX Reactor. Diesel flow rate 1 l/h, O₂/C and H₂O/C ratios of 0.5 and 3.5 respectively. Legend: Tm OSR, Tm WGSR, Tm PROX, H₂, N₂, CO, CO₂

Once the OSR was characterised, the WGS Reactor and later the PROX Reactor were connected. In Fig 8, temperature profiles and gas composition at the output of the WGS (a) and PROX (b) reactors are
presented. It can be clearly observed the transitory process in the reactors, which involves variations of gases concentrations to reach stationary conditions and a slight increase of reactors temperature up to their stable value.

In Fig 9 reforming gas composition at its crossing through the different reactors when they work in steady-state conditions are shown. Diesel flow rate was 1 litre per hour and oxygen/carbon and water/carbon ratios were 0.5 and 3.2 respectively. It can be seen how hydrogen concentration goes from 36.9 per cent at the output of the ATR to 43.2 at the outlet of the WGS, and how carbon monoxide decreases from 6.7 per cent to 0.3 due to the WGS reaction. At the outlet of the PrOx, the percentage of hydrogen decrease 1 per cent and the carbon monoxide is lower than 500 ppm. It is has to be remarked that values lower than 500 ppm could not be measured because the gas chromatograph used was not prepared for it. In next papers exact results will be presented.

4. CONCLUSIONS
An experimental facility for obtaining the necessary hydrogen to produce 5 kW of electric power in a PEM fuel cell has been developed. Working parameters and feeding flows of the ATR reactor have been adjusted. Nowadays, control strategies and PIDs of the whole facility are being tuned. Compositions and temperatures at the output of the ATR reactor have been obtained and validated with results from ICP-CSIC and other authors. For the decaline case, the optimum values of O2/C and H2O/C ratios (0.35 and 3 respectively) and the maximum decaline flow rate (1.5 l/h) have been obtained. With these values reformer efficiency is 69% with a performance between 0.90 and 0.91%. For the diesel case, the obtained values of outlet composition are similar to the obtained in bibliography. It remains to determine the optimum values of O2/C and H2O/C ratios, which according to the bibliography should tend to lower values [7-8], next to 0.3-0.35 and 2-2.5 respectively. Maximum performance, 87.5%, was obtained for an O2/C ratio of 0.45 and a H2O/C ratio of 3.

First tests coupling to the reformer gas cleaning reactors: desulphuriser, WGS Reactor and PROX Reactor has been accomplished, being the results similar to those gather in the bibliography. Nowadays, not only tests for characterising the reformer with diesel fuel are being carried out, but also tests for characterising the other reactors of the facility (WGS and PROX). Tests for integrating the reformer with a 5 kW fuel cell are also going to be accomplished. Tasks regarding the development of thermal integration, reduction of starting time, autonomy, design size reduction and increase of the produced hydrogen will be developed during the next year.

5. ACKNOWLEDGMENT
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6. REFERENCES
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