SUMMARY

The aim of the thesis is to study and evaluate a new process for the generation of hydrogen with intrinsic sequestration of carbon. More specifically, the research work is aimed to investigate the “chemical-loop” approach for the reforming of bioethanol into CO/CO₂ and H₂ produced separately. This would make the production of H₂ simpler and economically more convenient than it is currently done by conventional methane reforming. Moreover, an additional advantage in terms of sustainability is the use of bioethanol as the source of hydrogen, instead of natural gas.

During the first year a testing apparatus has been built up and calibrate, and several catalysts have been prepared, characterized and tested them as catalysts. This allowed us already to discriminate catalysts that will be deeper studied and will be improved. Different ways to improve the catalysts have already been envisaged and are currently applied for demonstration.
INTRODUCTION
The chemical-loop approach, already investigated in the literature [1, 2] for the transformation of natural gas, has never been applied to bio-alcohols although it would be well adapted and economically more favourable. The approach consists in separating the two distinct steps of a reforming process. The first step is the reduction of a mixed oxide material with bioethanol, with production of CO, CO₂ and H₂O. The second step is the re-oxidation of the reduced oxide with water, and generation of a concentrated stream of H₂. The aim of this research is to define conditions and materials that may lead to an optimized process, allowing producing a hydrogen stream that does not require any additional purification or separation treatment. A variety of materials reacts easily with water or acids to release hydrogen. However they have to be reduced to react again with water leading to a two-step cycle. The main advantages of thermochemical cycles are : 1) the possibility to obtain hydrogen separately from oxygen avoiding separation costs of the two gasses ; and 2) the possibility of reaching relatively high efficiency up to 50% or more [1]. Among the various thermochemical cycles, the mostly studied ones are those based upon pure and mixed iron oxides, because of their efficiency, which is comparable to the other compounds under examination, and a reducing temperature, which is relatively low. They are also cheap, easy to synthesize materials, and the flexibility of composition allows tuning the chemical-physical properties. Because of these reasons, metal ferrites have been chosen as oxygen/electron carriers for the cycle transformation of ethanol into hydrogen.

EXPERIMENTAL
Four different ferrites have been prepared: Fe₃O₄, CoFe₂O₄, NiFe₂O₄ and CuFe₂O₄ through a co-precipitation method [3] and calcined at 450°C. They have been characterized using several methods: XRD, BET, Mössbauer spectroscopy and TPR. The catalysts have then been tested on a homemade apparatus to study their behavior during the reduction with ethanol and characterized again after reaction. A schematic representation of this apparatus is given at the right of this text. The reaction conditions have been optimized and the best results have been obtained loading an amount of catalyst of 0.4 g with a flow of liquid ethanol of 0.52 ml/h and a flow of inert (N₂) of 30 ml/min with a time of contact of 0.21-0.26 s (with ethanol in gas phase). Tests have been carried out at 450°C for 1h and the products have been monitored in-line via micro-GC (for the non-condensable compounds) and off-line with GC-FID. Tests were carried out using an azeotropic mixture of ethanol/water (95.4/4.6 %), thus has been made for two reasons: (i) the availability of azeotropic mixtures and (ii) the possibility that the presence of water could help to oxidize the coke formed during the reaction. In fact it has been shown previously that the presence of coke is the main drawbacks in this kind of reaction, since if present during the oxidation step with water it will pollute the hydrogen produced.
RESULTS

The four different catalysts have been tested in the reduction step firstly to see the effect of the cationic composition of the ferrites and to decide which ferrite is the most promising. Results obtained are shown in the following figures:

![Graphs showing conversion and yields over time for FeFe450, CoFe450, NiFe450, and CuFe450 catalysts.](image)

From these tests has been possible to see the main differences among the various ferrites. It is possible to see how conversion’s trend increases in the order FeFe > CoFe > NiFe > CuFe especially in the first 30 min after whom all the catalysts exhibit a full conversion. H₂ is produced in high quantity since the first minutes of reaction with CuFe, while with the others it requires a certain time before reaching his highest yield. A common issue with all the samples tested is the production of a high quantity of coke, however there is a minimum in its trend between 5 and 10 min where its yield is around 30 %. Further tests have to be done to check if this short time is enough to reduce the catalyst to a reasonable grade, in this case it will not be necessary to perform the reduction for a longer time since it would lead to higher yields in coke. The others main byproducts obtained during the reduction are CO and CO₂ with different yields depending on the material. In the case of CoFe and NiFe water and CH₄ are produced with yields around 10 %, lower in the others. Other byproducts are present in smaller quantities, which are: acetaldehyde, ethylene, ethane, acetone, ethyl acetate and propylene. Tests are presently being performed feeding absolute ethanol to evidence the effect of the presence of water in the feed.

![Graphs showing CoFe reduced with azeotrope and absolute ethanol.](image)
The first results obtained with cobalt ferrite show that yields’ trends are similar, especially at longer time, while in the first minutes of reduction the conversion is total feeding absolute ethanol, while with the azeotrope about 25 min are required. Same behavior can be seen for the H₂ yield. After every test the reduced catalysts have been characterized again by XRD and Mössbauer spectroscopy. XRD patterns show that the ferrites have been partially decomposed and that iron carbide (Fe₃C) is formed. The formation of Fe₃C is lower at lower temperatures or when the samples are reduced with pure ethanol. These results have been confirmed by Mössbauer spectroscopy that allowed to quantify the relative amount of the different phases present and to calculate the reduction level of the solids. To illustrate these results, an example of material composition after the reduction is given in Table 1:

<table>
<thead>
<tr>
<th>Material</th>
<th>Reduction T (°C)</th>
<th>Feed</th>
<th>%Fe³⁺</th>
<th>%Fe²⁺</th>
<th>%Fe⁰</th>
<th>%Fe₃C</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeFe</td>
<td>450</td>
<td>Azeotrope</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>CoFe</td>
<td>450</td>
<td>Azeotrope</td>
<td>14</td>
<td>-</td>
<td>35</td>
<td>51</td>
</tr>
<tr>
<td>CoFe</td>
<td>400</td>
<td>Azeotrope</td>
<td>63</td>
<td>6</td>
<td>22</td>
<td>9</td>
</tr>
<tr>
<td>CoFe</td>
<td>450</td>
<td>Absolute</td>
<td>8</td>
<td>-</td>
<td>74</td>
<td>18</td>
</tr>
</tbody>
</table>

Presently the reoxidation of ferrites by water is under study. Preliminary results show that depending upon the degree of reduction a more or less complete re-oxidation of the catalysts to the initial ferrite can take place. However coking and Fe₃C formation during oxidation lead to CO₂ polluting the hydrogen formed during the re-oxidation. The results obtained up to now also show that the specific surface area of the catalysts has been reduced after the first cycle.

CONCLUSIONS AND CURRENT DEVELOPMENTS

Results show that ferrites can be used for the chemical loop process of production of hydrogen from ethanol. The best conditions for running the reduction’s step have been determined. Still the duration of this step has to be optimized to reduce as much as possible the formation of coke. A small amount of water added to the feeds does not help to reduce such formation and had also a negative effect. Furthermore a sintering process of the catalysts has been evidenced that is detrimental to its activity. New solutions are already under study to reduce the formation of coke and the sintering of the catalysts. Ce and Zr supports are known to help for oxygen mobility and resistance to sintering and carbon deposition [4]. A copper ferrite supported on Ce-Zr has already been prepared and ready to be tested. Another kind of support took in consideration is carbon nanotubes [5]. A NiFe₂O₄ supported on carbon nanotubes has already been synthesized together with a CoFe₂O₄ which has also been tested, but they need further analysis. However the results obtained seem to be very promising. Another possibility is in the introduction of very small amount of Rh in the catalyst. Rhodium is known to help in the reduction step of iron based catalysts and should also be helpful in the oxidation of coke. Studies made by us show that at 400°C its oxidation can be complete and catalysts of this kind will be prepared soon.

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REFERENCES