

Interaction of CO₂/CH₄ with steel wool in an electrocatalytic dry reforming reactor

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Abstract

Dry reforming is a process allowing simultaneous conversion of hydrocarbons (methane being the prototype molecule used for this study) to syngas using carbon dioxide as an oxidizing agent. Such strategy may eventually become an opportunity for the industrial sector to produce syngas whilst valorizing residual CO₂. As reported previously, an iron-based catalyst, i.e. steel wool, activated by an electrical current showed potential for dry reforming. As a follow up to this preliminary work, this study mainly focuses on the characterization of the low-cost thin iron wires in order to determine the robustness and stability of the iron material over extended operation. Under CO₂/CH₄ molar feed ratios ranging from 0.8 to 1.25, coking is inhibited by high surface temperature. After 25 hours of operation at a temperature higher than 900°C measured in the gas phase, XRD patterns show a preserved Fe structure along with FeO suggesting an eased redox cycle with CO₂ and CH₄. It is also showing that a high CO₂/CH₄ ratio favors higher oxidation states of the iron in the zone of the iron bed, which is first in contact with the gas input. Decreasing the temperature to 800°C favors oxidation by CO₂ over reduction by CH₄ leading to Fe₃O₄ formation. This disturbs the Joule dissipation through the wire mesh catalyst bed. Although high molar ratios of CO₂ over CH₄ result in fast oxidation of the catalyst, reducing the ratio may lead to increasing the catalyst lifespan which, overall, is essential to scale this process to a commercial scale.

Keywords: carbon dioxide, dry reforming, iron, syngas, methane.



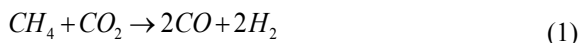
1 Introduction

Carbon dioxide has increased dramatically in the atmosphere during the last centuries making it one of the prior concerns of the international community for the upcoming years [1]. In order to control the emissions of carbon around the globe, different countries are putting forward the concept of carbon credits where the companies emitting large amounts of carbon would be charged by mass unit of carbon emitted to the atmosphere. At this point in time, carbon credits are creating a value for CO₂ for which the price varies from -15USD [2] to -23USD [3] per ton. This incentive has two effects, on one hand, taxation of the CO₂ emitted should to a certain extent limit the emissions whilst on the other hand, it also provides a tipping fee for this carbon source which could then be considered as a feedstock.

Whilst first generation biofuels aims at using edible feedstock (as sugarcane, corn or oily seed), second generation is related to the usage of lignocellulosic biomass whilst the third generation biofuels are for most experts related to algae [4]. The latter, on the other hand are not a feedstock on their own but relies on the uses of CO₂ as carbon source thus making of carbon dioxide, to a certain extent, the cornerstone of third generation biofuels.

Despite the fact that it is abundant everywhere in the world and that it is a renewable source of carbon, CO₂ is also the most oxidized and stable form of carbon. Production of carbon dioxide usually generates energy and converting the latter back to valuable compounds should also require comparable energetic investment. Production of algae from this carbon feedstock is of course a very tempting approach since the sun would provide the energy required to reduce carbon dioxide ultimately. Linking the production of algal biomass with large CO₂ producing facilities is also an approach that is gaining significant interest since carbon dioxide is harvested directly from an abundant source, the industrial flue gases. However, the sun is not the only source of energy that could be used for the reduction of CO₂ and the latter could as well be converted using chemical process [5] or even thermal processes [6].

Nevertheless, at the bottom line, the important factors that could lead to the conversion of CO₂ are the efficiency of the process and its overall economical balance. Of course, the energy balance is also a significant concern as well as the nature of the energy, which should ideally be produced with minimal amounts of emitted CO₂. Recently, our team has reported on the dry reforming of methane and CO₂ in an electron-activated iron catalytic bed [7]. Using hydroelectricity, a green energy abundant in many regions of the world including in the province of Quebec (Canada), methane (that could come from biogas, flue gas, or even tail gas of second generation biofuel processes) was oxidized to syngas using carbon dioxide as oxidant as depicted by the reaction below:



The possibility of using hydroelectricity is of interest since the use of such form of energy could replace part of the hydrocarbons that provide the heat needed to overcome the endothermicity of the reforming reaction and may lead

to a process that would have a very low carbon footprint. Nevertheless, reforming methane with carbon dioxide is a very challenging concept since the process should combine high conversion of the methane, high energy efficiency and low deactivation rates of the catalyst.

In this report, focus will be made on the interactions between methane, carbon dioxide and the metallic iron that acted as a catalyst in the experimental setup.

2 Materials and experimental details

2.1 Experimental setup

The flow diagram of the experimental setup as well as the detailed continuous electrical dry reforming reactor's geometry is illustrated in Figure 1 below (for more details on the experimental setup see Labrecque *et al.* [8]). The interior volume of the reactor was of 235 cm³ with one steel electrode on each end. The working part of the reactor was inserted in an Al₂O₃ refractory cylinder to thermally insulate the catalyst from the outer shell of the reactor (made of stainless steel). The electrodes were electrically insulated from the steel reactor shell by custom-machined Teflon[®] fittings on both steel insertion tube ends. Inside the reactor, void spaces between the refractory cylinder and electrodes were further insulated with Kaowool[®] Flex-Wrap high purity ceramic fibres

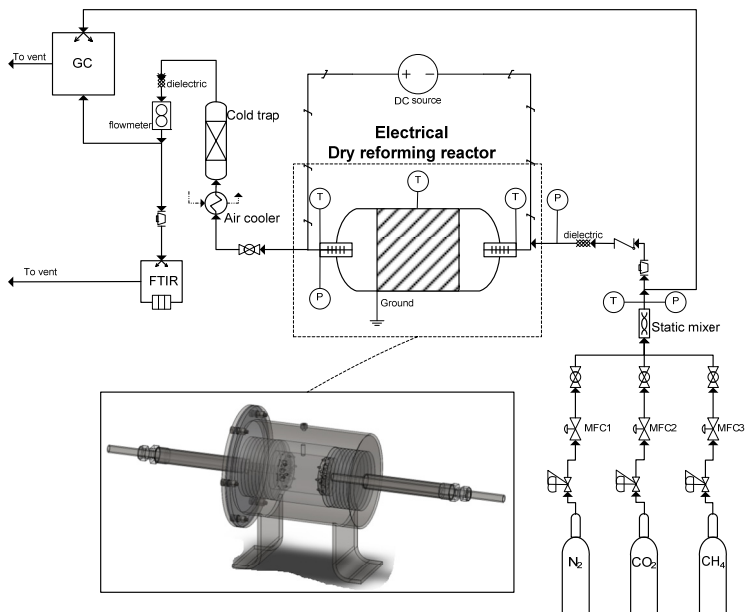


Figure 1: Experimental flow diagram.

paper ensuring off gassing at a minimum. The reactor is connected to a direct current (DC) power supply with adjustable voltage (0–12V) and amperage (0–500 amp) allowing the reactor to be solely heated via the Joule effect, therefore, the catalyst's bed configuration is known to have a direct impact on the heating properties of the experimental setup. The desired feed injection (volumetric flow of N_2 , CO_2 and CH_4) were regulated by three thermal mass flow controllers (MFC) SLA-5850 purchased from Brooks Instrument and calibrated for their respective gases. The feed stream was injected through the electrode's tube before diffusing in the catalytic media. Most of the water contained in the outlet gas flow, which is formed in most cases while operating the reactor was condensed in a cold trap. The outlet gas composition was then analysed by at-line Gas chromatograph Bruker 456-GC and correlated with a FTIR Varian 640-IR. Real time temperature and gas flow monitoring of the overall system was done using National Instrument Data Acquisition System NI cDAQ, which was linked to a Labview programmable interface. The inlet and outlet thermocouples were positioned in the electrode's hollow tubes close to contact points. A central thermocouple is also fitted in the catalyst's core and the latter was, as all the other used in this system, insulated with ceramic sleeves.

2.2 Catalyst medium

In this work, Bulldog[®] steel wool was used as catalyst for the electro-catalytic dry reforming of methane. The element analysis performed on the steel wool previously indicated that it was composed of iron at 98.5%, 0.24% carbon as well as minor impurities [8]. For each experimental set reported in this work, 32 grams of coarse grade (No. 0) steel wool were used. Steel wool was used as is in the dry reforming reactor without any chemical or thermal treatments whatsoever. Before insertion in the reactor, the packaged steel wool mats were unrolled and cut in layers of 7 cm long along strands orientation. All layers were stacked and rerolled to form a uniform conductor with steel fibers parallel to the gas flow and electric current direction. The uniformity of the catalyst bed is important to minimise electricity's channeling through the catalyst, which lead to hot spots formation affecting the packed bed integrity and thereafter inhibits stable operation conditions.

XRD pattern for the initial steel wool before reaction is shown in fig. 2 and shows that the crystalline structure of the iron steel wool is essentially composed of α -ferrite showing that the initial passive oxide layer is not visible on the actual XRD pattern. SEM-EDX analysis on an initial strand confirms a surface composition of Fe, O, C, Mn, Ca with traces of impurities typical to steel.

SEM images of steel wool before reactions (fig. 3) shows the microstructure resulting from the industrial shaving process commonly used to produce steel wool [9]. A characteristic single strand reveals a "smooth" surface on one side and a "torn" surface on the reverse side. Shaving blades scratches may be observed on the smooth face.

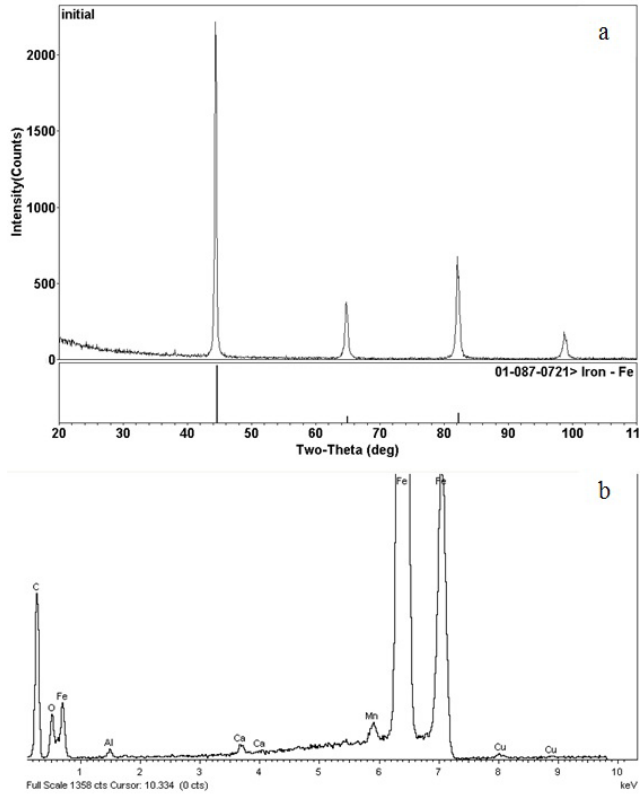


Figure 2: (a) XRD analysis of steel wool before reaction. (b) SEM-EDX analysis of steel wool before reaction.

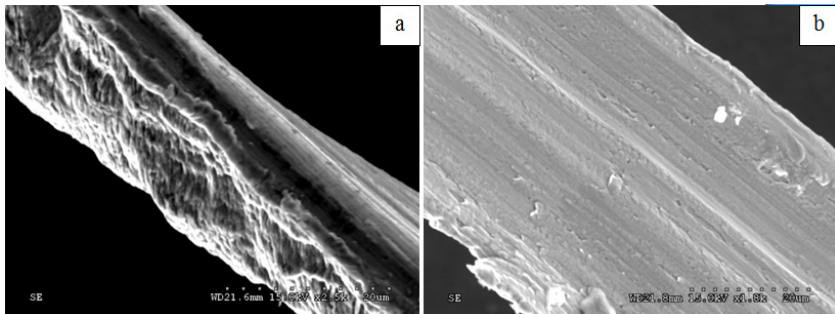


Figure 3: SEM images of steel wool before reaction: (a) side view of a single wire, (b) "smooth" surface of a single wire.

2.3 Characterisation of the catalyst

The post-reaction crystalline structure, composition and morphology were analysed by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Data from the latter were obtained with a Panalytical X'pert Pro diffractometer using Cu α radiation at room temperature using a sample stage spinner along with X-ray tube settings of 40 kV and 50 mA. All samples were scanned from 25° to 110° (2 θ) with a step size of 0.060° and counting time of 3 seconds. Each iron bed catalyst passed to XRD were analysed in two parts. The “inlet” end of the catalyst, which represents the first layer of 1 cm long in contact with the inlet electrode (feed point of the gas stream) was analysed separately from the outlet end, which is the last 1 cm layer in contact with the outlet electrode (exit point of the gas stream). The diffraction patterns were then compared to explicit variations between both ends of the catalyst.

SEM pictures were taken with a Hitachi S-3000N using secondary electrons imaging mode. A Hitachi S-4700 field emission gun coupled with energy dispersive X-ray spectroscopy (EDX) has also been used for Fig. 2.

2.4 Experimental conditions

As for the experiments that are listed in Table 1, high temperature (HT) and lower temperature (LT) sets have been conducted over intermittent runs composed of 4–5 runs of 5 h (average) exposed to the reactive gas mixture. For HT run the amperage value was set to 195 A. For LT experiment the amperage value was lowered progressively while running to keep an average temperature of 800°C. The reactor was preheated under nitrogen (N₂) with a inflow of 500 ml/min until a temperature of 950°C was reached for HT experiments and up

Table 1: Dry reforming test run description. HT stands for “high temperature” and LT stands for “lower temperature”.

| Run | CO ₂ ctrl. | HT1 | HT2 | LT3 |
|---|-----------------------|---------|---------|----------|
| Ratio CO ₂ /CH ₄ | CO ₂ only | 0.8 | 1.25 | 0.8 |
| Temperature (°C) | 870–920* | 930–950 | 935–945 | 790–860* |
| Current I (amps) | 170–50* | 195 | 195 | 170–120* |
| Total flow (ml/min) (T ^{ref} 22°C) | 1000 | 1800 | 1800 | 1800 |
| Total run time exposed to reactives CO ₂ /CH ₄ (h) | 1.2 | 25 | 23 | 20* |

*Larger range of temperature and amperage value for LT experiment are due to less stable operating conditions of the electrical reactor while the global conversion of CO₂ and CH₄ are low. Actually, the heat of reaction (overall endothermic) “auto-regulates” the system as the overall resistance of the catalytic medium is affected by the temperature of operation.

to 750°C for LT experiments. Once at the operating temperature, the CO_2/CH_4 ratio was adjusted to the desired value using a mass flow controller. At the end of each run, the reactor was cooled down under a N_2 flow of 500 ml/min until a temperature of 300°C was reached. The CO_2 control experiment was performed in a single run only as a result of a forced complete shutdown of the system, which means that after one hour running under these conditions, the electrical contact between the electrodes has been lost. For the CO_2 control experiment, the amperage needed to be lowered progressively while running.

3 Results and discussion

3.1 CO_2 control experiment

Passing a flow of 1000 ml/min of CO_2 only through the iron bed resulted in fast oxidation of the iron ending in a complete loss of the integrity (initial structure) of the iron bed that became brittle after reaction. During operation, the resistance of the iron bed was increasing constantly as a result of oxidation. For a set amperage value, the increasing resistance was depicted by an increase of the measured voltage. The changing voltage value was probably related to an induced channeling of the current through the remaining metallic strands as oxidation was progressing into the network.

The XRD data (fig. 4) shows that the initial characterised α -ferrite peaks were essentially converted to magnetite Fe_3O_4 . Ferrite peaks positions are denoted by fig. 4 although the latter are not further observed on the XRD analysis. It was noted that total oxidation of the catalyst bed was achieved after 1.2 hours of operation. The oxidation potential of carbon dioxide on the iron bed was then

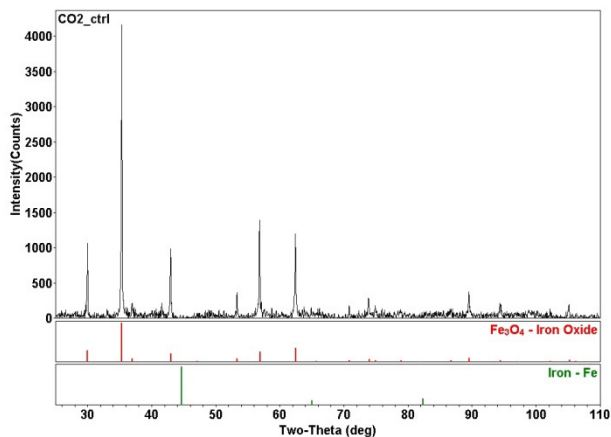


Figure 4: XRD analysis of the iron bed after complete oxidation by CO_2 .

demonstrated as a potential hindrance to stable operation of the electrical reactor. If iron is used as a catalyst instead of a consumable, the presence of a reducing agent becomes essential to preserve catalyst's integrity.

Furthermore, the oxidation has led to CO production showing the potential of iron as reducing agent for CO₂. A general concern in CO₂ reduction processes is the control of the degree of reduction. CO₂ reduction may result either in partial reduction to CO or complete reduction to elemental carbon. In our case, no carbon formation was observed. Only CO production and magnetite Fe₃O₄ formation were detected for the CO₂ control experiment.

It can be shown by Gibbs free energy minimisation calculations that in large excess of CO₂, complete conversion of Fe to Fe₃O₄ is expected. Likewise, operating at temperature higher than 700°C generally result in partial reduction of CO₂ with 100% selectivity to CO no matter if Fe is oxidized to wustite (FeO) or magnetite (Fe₃O₄) [10].

In addition, it must be noted that no carbon formations were depicted on the surface of iron strands for all experiments discussed in this work. It was supposed that high surface temperature (>900°C) of the heated iron bed related to Joule effect inhibits coking formation. Despite the fact that Fe is known to favor carbon formation and moreover multivalent iron oxides (magnetite) are known to catalyse the Boudouard reaction [11], the latter reaction is thermodynamically inhibited at temperature higher than 820°C and atmospheric pressure [12].

Another possible source of coking formation that could be expected might be the occurrence of methane thermal cracking. Iron based catalysts generally have an activation temperature for methane catalytic cracking ranging from 700°C to 950°C [13]. High surface temperature of the iron bed might then in some cases favor carbon deposition by methane. However, all experiments were conducted with O/C ratios close to 1 which contributed to minimize carbon formation. Indeed, presence of CO₂ may contribute to help “clean” the surface from C via the reverse Boudouard reaction [14].

3.2 HT1, HT2 and LT3 experiments

Under HT1 conditions, the reactor was extensively stable for the entire length of the experiment. Steady state conversion regime was easily obtained and electrodes had a good contact with the catalyst for the whole experiment. XRD pattern comparing the inlet end and the outlet end of the catalyst are almost identical for the HT1 test. The α -Iron peaks were quite preserved and slight formation of wustite (FeO) was observed (Fig. 5(a)). CO₂/CH₄ feed ratio of 0.8 showed a potential to preserve the iron bed structure. At high temperature, the decomposition rate of CH₄ over the surface accompanied by further reduction was sufficient to protect the iron bed from complete oxidation by CO₂. The catalyst structure was then stable over the whole 25 hours period exposed to the gas feed mixture. Furthermore, it has been reported that FeO is subject to significantly increase CH₄ conversion with CO₂ [15]. The observed FeO on the iron bed's surface might agree with an enhanced interaction with the gas mixture feed stream.

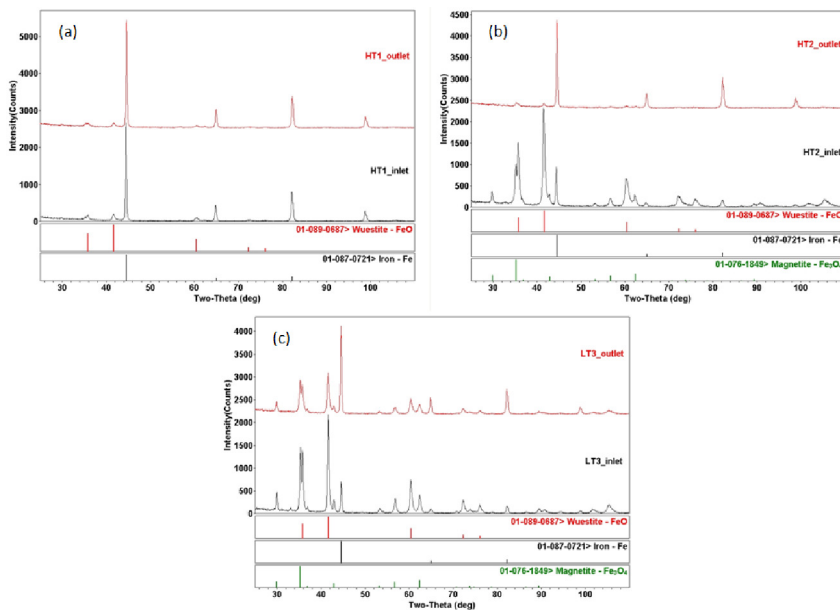


Figure 5: XRD data of (a) run HT1, (b) run HT2 and, (c) run LT3.

Running under oxidizing conditions (HT2) has resulted in inhomogeneous iron bed structure when comparing the inlet and outlet end sections as depicted by the XRD results shown in figure 5(b). The inlet was overall oxidized at a higher level resulting in Fe_3O_4 and FeO as main oxides in contrast with the outlet end that showed a preserved iron phase and a slight formation of FeO similar to HT1 results. Even though a more oxidizing feed ratio was used (1.25), the conversion of CH_4 reached at 900°C was sufficient to preserve the catalyst's outlet from oxidation. However, such a contrast in oxidation level is mainly explained by the fact that the oxidation kinetic of the catalyst by CO_2 is faster than reduction mechanisms of the catalyst by CH_4 . It is often reported that the rate limiting step for methane activation, a key step towards hydrogen formation from natural gas, is the dissociation of CH_3 to CH_2 and H [14]. In addition, it is noted that the oxidation rate of the inlet was expected to be proportionally governed by the CO_2 partial pressure of the gas feed mixture [16].

In such conditions, an oxidizing front is then moving in the direction of the gas along the iron bed implying a form of deactivation. The later situation would be expected to be increased at higher CO_2/CH_4 ratios. Operating the reactor with a reducing feed stream is then suitable to minimise the formation and evolution of such an oxidizing front that contribute to decrease the lifespan of the iron bed. Furthermore, as opposed to FeO , Fe_3O_4 is not recognized as a good oxidant for methane reforming [17] and its formation might decrease reactor's overall efficiency.

Regarding the low temperature experiments (see LT3 on Fig. 5(c)), magnetite (Fe_3O_4) and wustite (FeO) were formed on both ends of the catalyst at lower

temperature (average 800°C). Again in that case, the iron phase was more preserved at the outlet than at the inlet. FeO and Fe₃O₄ relative intensities depicted for LT3 are however really similar for both inlet and outlet pattern. Same conclusion emerges that the temperature must be sufficiently high to activate CH₄ decomposition whilst competing with CO₂ oxidation. However, looking only at oxidized end (inlet end) for HT2 and LT3, the oxidation level was higher for LT3 (800°C) even though a more reducing CO₂/CH₄ ratio was used for the latter. The reactor's flow configuration give rise to a gas-solid contact pattern which results in an effective over-stoichiometric supply of CO₂ for iron oxidation.

Furthermore, distinct morphology characteristics of the oxides formations observed by SEM comparing an inlet section steel wool strand with an outlet one from HT2 experiment is shown in Fig. 6. The apparent oxidized structure differs for the two oxidation level. At higher oxidation state (a), crystallites are more developed and spread over the iron fiber. The outlet end (b) mainly composed of FeO surface is characterised by fine stacked layers of crystals.

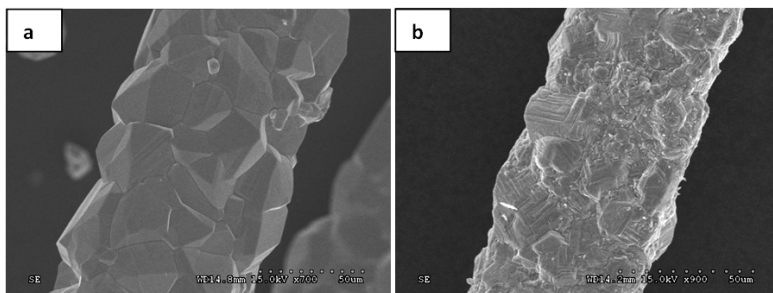


Figure 6: Difference in oxides formation morphologies from HT2 experiment: (a) inlet end; (b) outlet end.

4 Conclusion

In this work the interaction between the inlet gas and the catalyst was studied for a dry reforming reaction under an electron-activated steel wool catalytic bed. The CO₂/CH₄ as well as the temperature had a significant impact on the lifespan of the catalyst ranging from 25 hours at high temperature with a ratio of 0.8 up to less than an hour when pure CO₂ was injected in the reactive system. Increasing the ratio over 1.25 has lead to a rapid oxidation of the catalyst at high temperature (over 900°C). As for lower temperature (below 900°C) oxidation of the catalyst was more pronounced that over 900°C showing that the reactions involved in the system were unbalanced in favour of oxidation of the iron. At higher temperature, an excess of methane showed to have a positive effect on the catalyst maintaining it for a longer period of time. The oxidation pattern in the catalyst bed showed to be a gradient and the oxidation level of the steel wool used in this experiment was more pronounced at the gas inlet when compared to the gas outlet.

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