

The use of catalytic reforming reactions for CO₂ sequestration as carbon nanotubes

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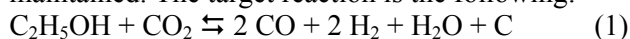
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Abstract: - Carbon sequestration is one of the proposed solutions for the decrease of atmospheric greenhouse effect gases (GHG). Recent works of the authors produced a related patent and proved that catalytic dry reforming of fossil or renewable fuels (i.e. natural gas, biogas and ethanol) can achieve this goal. Although the energetic efficiency of the process is about 50% lower than that of the classical steam reforming route, the high added value nanotubes produced at relatively low temperatures (below 600°C) and atmospheric pressure offset this disadvantage. This work proposes a carbon sequestration process under the form of valuable MWNT (Multi-Wall Nano-Tubes), based on the use of activated carbon steels as ethanol dry reforming catalysts. This experimental work provided the authors with the necessary information to undertake and present here a techno-economic feasibility study at industrial level based on a preliminary engineering analysis.

Keywords: - Carbon Sequestration, GHG, CO₂, Dry Reforming, Catalysis, Carbon Nanotubes, MWNT

1 Introduction

This work undertakes a preliminary evaluation of the techno-economic feasibility of a process using CO₂ to simultaneously reform ethanol and sequester a GHG under the form of valuable carbon MWNT. One of the process basic characteristics is the use of catalysts that a) favour the formation of filamentous carbon (carbon nanotubes), and b) have no internal surface such that the carbon formed can be readily removed while their activity and integrity is maintained. The target reaction is the following:



From the above quoted reaction, it can be seen that the target is the formation of carbon, in an amount equivalent to that of the CO₂ used. In these circumstances, the dry reforming process produces less synthesis gas than that obtained in the full reforming reaction but it sequesters the CO₂ carbon in an inert solid form, readily removed from the non-porous catalytic surface. If the commercial value of the carbon sequestered in this way is proved high enough, it could constitute the major revenue source for the project; the other revenue sources would be a) the synthesis gas as energy vector or raw material for liquid fuels synthesis and b) the credits from the carbon sequestration.

2 Literature

Few works [1,2] are available in the literature regarding the dry reforming of ethanol. Tsiakaras and Demin [3] studied the thermodynamics of ethanol reforming by CO₂, but they did not perform any experimental work.

Ruckenstein and Wang, 2002 [4] indicate that the main drawback of this process is that the carbon dioxide reforming leads to the formation of inert solid carbon, this can then deactivate the catalysts used. In a previous work [5] the authors proved that a simple iron based non-porous catalytic formulation allows us to produce carbon MWNT altogether with the reforming without harming the catalytic properties. This is done at the expense of the iron catalysts, which are consumed as nanograins inside the MWNT but the low cost of the catalyst does cause significant concerns.

3 Methodology

The experimental work was done in a) an appropriately equipped continuous flow isothermal fixed-bed reactor set-up coupled to a GC analyzer shown in Fig. 1 and b) a multi-differential isothermal reactor set-up coupled to a Quadrupole MS analyzer, shown in a previous publication [5]. The mass and energy balances allow the calculation of the energetic efficiency of the reaction as well as the quantification a) of the gaseous fuel (CO+H₂)

produced and b) of the mass of the carbon nanotubes. The catalysts used are activated iron alloys without internal surface. The morphology and composition of the carbon MWNT have been evaluated through FEG (Field Emission Gun) and TEM (Transmission Electron Microscopy).

The results include a fuel and CO₂ conversion efficiency as function of the catalysts used, the temperature, the ratio fuel/CO₂ and the feed spatial velocity. The regenerability of the catalytic surface after the carbon removal has also been tested and reported. Although these catalysts are consumed during the reaction through the formation of nano-grains inside the MWNT the rate of consumption and the cost of these catalysts are both low, thus rendering this cost item negligible.

4 Results

This section presents the results obtained in both experimental set-ups using carbon steel 1008 as catalyst.

4.1 Differential reactor

The isothermal differential reactor is loaded with the catalyst pellet or pellets and is fed with the appropriate mixture while the temperature programmed furnace is switched on. For the runs performed with non-pretreated carbon steel the temperature is raised at the set point under a pure Argon flow and once the temperature plateau is reached the reactants mixture is fed in the reactor. The Quadrupole MS samples the outlet of the reactor continuously and the readings (current intensity) are recorded. Since these runs are exploratory there are no full mass and energy balances; the readings appearing in the Figures are current intensities normalized at a 0-100 scale.

4.1.1. Experimental runs with thermally activated and non-activated Carbon steel

Fig. 1 shows the dry reforming of ethanol with carbon steel 1008 for 3h. The carbon steel pellets used had a thickness of 1.6mm and diameter of 12.7mm. In this experiment there have been two pellets used one after the other, like two consecutive in series differential reactors separated by a film of quartz wool. The ethanol line is not shown because its MS signal was very high, thus coinciding with the point 100; the signals of the expected products from the reforming are overlapping around the point 10 which is essentially expressing the 0% concentrations. An examination of the steel surface after its use in this experiment shows no traces of

deposited carbon and the surface remain clean and metallic Fig. 4, which is commented in details at point 4.1.2, presents the results of the blank experiment which gives results similar to those obtained in the experiment with non activated Carbon steel. It is, thus, concluded that, under these conditions both the cracking and reforming activity of the carbon steel are close to zero. The traces of reforming products detected in both runs are most probably due to some thermal cracking activity.

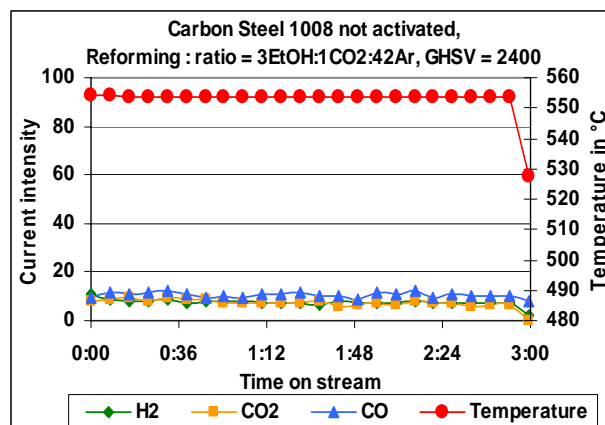


Figure 1: Dry reforming with inactivated carbon steel

Fig. 2 and 3 are obtained from two experimental runs performed exactly at the same conditions for reproducibility purposes. These experimental conditions are similar to those in the previous runs (see Fig. 1 and 4) but with carbon steel pellets thermally pretreated (activated) at 800°C for 1hour in chromatographic grade Ar. These experiments are commented below:

- There was no significant ethanol signal detected at the reactor outlet (less than 10% of the signal observed on the blank) for the entire duration of the runs;
- The recovered carbon at the surface of the pellets was 25 and 29% of the CO₂ carbon content for Fig. 2 and 3 respectively;
- The apparent hyper-activity of the carbon steel at the end of the run in Fig. 2 is for the moment difficult to explain; the most reasonable explanation is a change of the EtOH/CO₂ ratio (probably more EtOH entering the reactor) which leads to higher carbon deposition and synthesis gas (H₂+CO) production.
- Since the target is to convert all of the carbon contained in the CO₂ molecule into carbon nanotubes the experimental conditions need to be optimized.

It is clear that the thermal treatment of the carbon steel induces some important changes which render the steel catalytically active. This is a very important

result because, as it will be also shown below, a cheap material (carbon steel) without internal specific surface, presents an excellent catalytic activity at very high space velocities. However, this catalytic activity is not yet fully identified; cracking and reforming are two different reactions and their role must be elucidated in the following steps of this work.

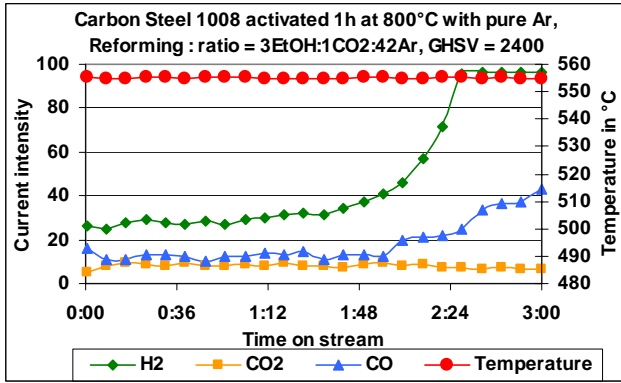


Figure 2 : Dry reforming with activated carbon steel

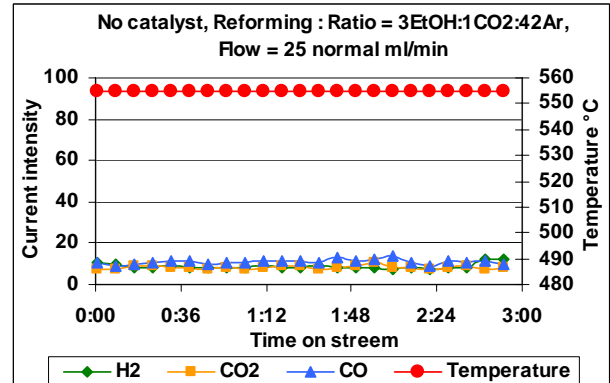


Figure 4 : Dry reforming without catalyst

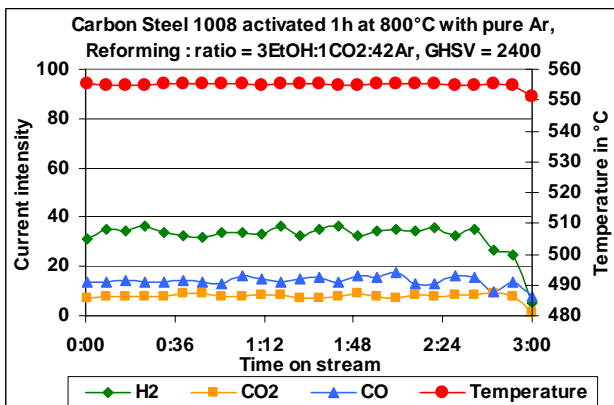


Figure 3: Dry reforming with activated carbon steel

The relatively low GHSV of $2\ 400\text{h}^{-1}$ based on the mass of the catalysts and the gas fed hides an important fact; the carbon steel tablets are not porous. Their specific surface is in the range of a few cm^2/g , not accurately measured by the BET method. Based on the surface calculated geometrically (2 times the surface of a circle of diameter 12.7mm for each pellet) the space velocity is as high as $720\ 000\text{ml}(\text{reactants})/\text{h}\cdot\text{m}^2$ which corresponds to a much more interesting flow rate for an eventual industrial application.

4.1.2. The blank experiment

The design of the differential reactor set-up allows the use of 5 differential reactors in parallel (5 parallel streams). During each experimental run, we

used 4 differential reactors with catalyst pellets and one blank. The blank has no catalyst, but the gas stream follows the same pathway and is submitted to the same reaction conditions as the other gas streams. Fig. 4 shows the typical results obtained from such a blank run. It is clear that there is no significant cracking or reforming activity under these conditions without catalysts.

4.2 Fixed-Bed reactor

The experiments shown in Fig. 2 and 3 have been reproduced at larger scale and at slightly different conditions. The reason being a) to make the proof that a scale-up is possible; b) to prove the activity of the thermally pretreated carbon steel and c) to see the effect of the EtOH/CO₂ ratio. A block diagram of the experimental set-up is shown in Fig. 5. The catalyst used was carbon steel shim stock (whose content in carbon is 0,13%) of 0.13mm thickness. This carbon steel was thermally pretreated (activated) at 800°C for 1hour under an inert atmosphere (Ar). The reactants molar ratio was of 2EtOH:1CO₂; there was no dilution with Ar, and the temperature was 550°C. The flow rate of the reactants were 145 NmlCO₂/min and 0,7ml of liquid ethanol /min. The experiment has shown a high reforming activity and, after 1h on stream, we have recuperated 4,5g of carbon, which corresponds to a sequestration rate of 105% of the CO₂ carbon content. This result is very promising since the optimal carbon yield is already reached with a non optimized yet reactor configuration. Additional work is needed to optimize the reforming yield and consequently the energetic efficiency of the process.

4.3 The carbon nanotubes

Fig. 7, 8 and 9 are typical examples of the carbon nanotubes obtained from the dry reforming of ethanol.

Fig. 7 depicts an image taken by SEM; it shows that the carbon nanotubes have diameters ranging between 15 and 40nm and various geometries, from rectilinear to spinal. Their ability to be bent without being broken is an indication of an interesting elasticity.

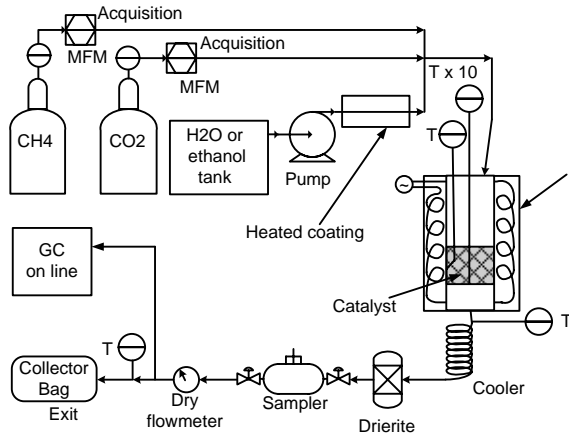


Figure 5: Dry Reforming Set-up

Fig. 8 is an image taken by TEM; it shows the structural elements of the nanotubes walls as well as the central hollow cylindrical tube. It is clear that the walls are built by structured parallel layers.

Fig 9 is an image taken at lower resolution by SEM; it presents a “forest” of aligned nanotubes arising from the surface of the catalyst. This picture is essential since it gives the proof of the catalytic nature of the nanotubes formation; the more blank (shining) points, appearing usually at the upper tip of the nanotubes are due to iron nanograins, which are thought to be the catalytic site at which the reaction is initiated. This is a mechanism similar to that occurring with Ni catalysts [6].

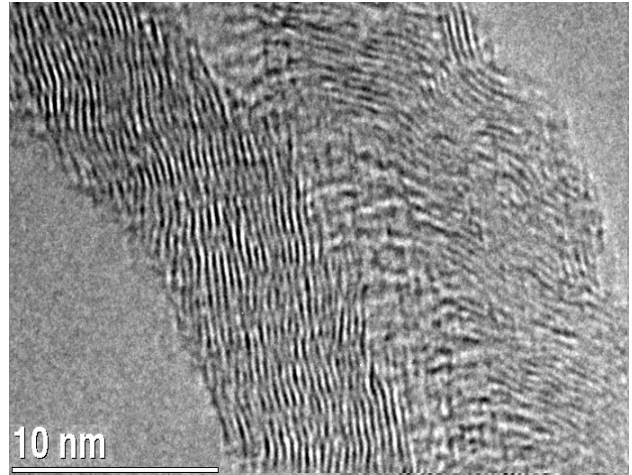


Figure 8: A Transmission Electron Microscopy (TEM) image of the Carbon MWNT

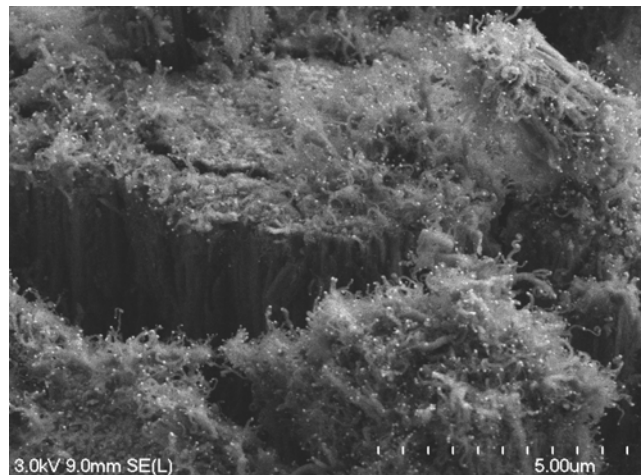


Figure 9: A lower resolution Scanning Electron Microscopy (SEM) image of aligned Carbon filaments

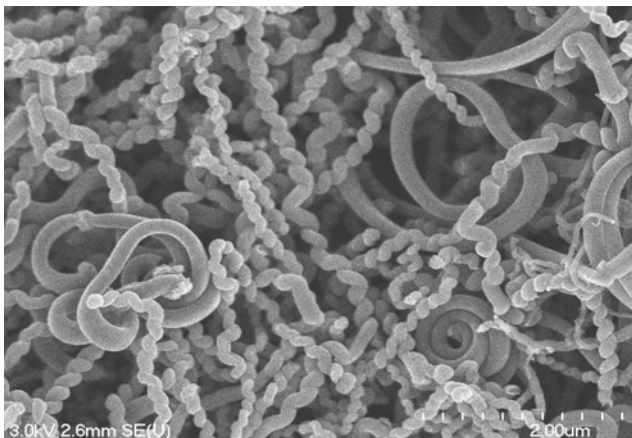


Figure 7: A Scanning Electron Microscopy (SEM) image of the Carbon MWNT

5. Industrial Production of Carbon MWNT by the DRIVE2 Process

The encouraging results of this work are at the basis of the DRIVE2 Process [7]. A Block Diagram of this process is presented in Fig. 6.

Table 1: Energy balance for Equation (1)

Basis : Ethanol entering the reactor (kg)	100
CO₂ entering the reactor (kg)	95.6
Sequestered Carbon out (kg)	26.1
Energy in (MJ)	2971.7
Reforming Losses (MJ)	362.8
Energy out (CO+H ₂) (MJ)	2473.2
Energy out C (MJ)	861.3
Energetic Efficiency (%)	74.2
Energy per kg sequestered C (MJ/kgC)	46.9
Energy per tn sequestered CO ₂ (MJ/tnCO ₂)	12791
Cost (US\$/tnCO₂)	112.7

Table 2: Energy cost of Carbon MWNT formation

1. Electrical energy production	Values	Units
Carbon Higher Heating value	33	MJ/kg C
Equivalent energy in kWh electric (combined cycle)	4.6	kWh/kg C
Cost of electricity production	0.04	US\$/kWh
Break-Even price of sequestered carbon	0.18	US\$/kg C
2. Steam production		
Carbon HHV	33	MJ/kg C
Cost of equivalent steam	0.004	US\$/MJ
Break-Even price of sequestered carbon	0.18	US\$/kg C

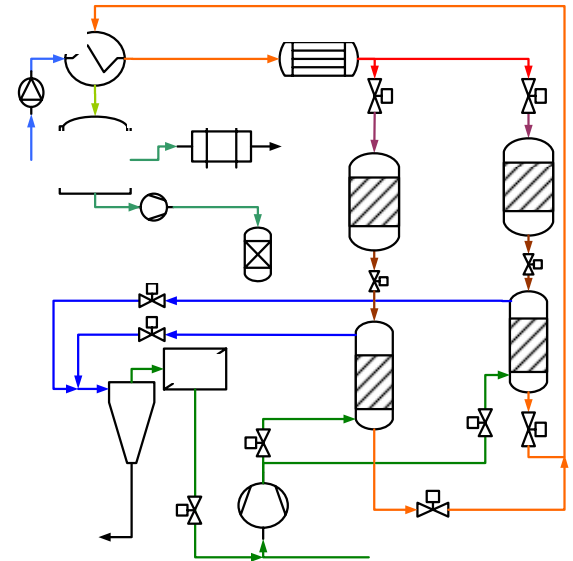


Figure 6: The DRIVE2 Process

The process is based on a twin-fixed bed reactors set-up producing the carbon MWNT and the synthesis gas. This configuration allows a continuous operation since one reactor is operated while the second one is emptied from the MWNT and regenerated before reuse. The other operations include heat exchange optimization, gaseous product purification and use as an energy vector according to each case needs.

If the process is operated within an existing plant the additional infrastructure cost for this operation is marginal and the real additional cost comes essentially from the energy consumption of the process. An energy balance on the reaction represented by Equation 1 is presented in Table 1, while Table 2 shows the energy cost of the carbon MWNT production. According to these results the energy cost of the Carbon MWNT production can be offset by a Carbon MWNT selling price of 0.2US\$/kg of sequestered carbon as MWNT. Besides, assuming that the carbon MWNT have zero price at the market, the process would necessitate a price close to 100US\$/tn of sequestered CO₂ to offset the energy cost of the carbon MWNT production.

6. Conclusion

This work has shown that the carbon contained in the CO₂ molecule can be sequestered by means of a catalytic reforming reaction. Ethanol was used as the basis fuel in this reforming study but other fuels can be used as well. Additional testing is required. The results are very encouraging and show that:

- A cheap and widely available material, a carbon steel, can be used efficiently as reforming catalyst after a thermal conditioning step; the reason of this material activation is not known and additional work is actually underway.
- This catalyst has been used in a differential reactor set-up for making the proof of concept. The results show that, under the testing conditions, the reforming is clearly catalytic and no cracking or reforming activity was found under thermal conditions.
- The process was scaled-up at bench level, where the experiments were performed with no Ar-diluted reactants mixtures. The results show that the effort was successful and that the carbon sequestration as MWNT was optimized easily (105% of the carbon contained in the CO₂ was recovered as MWNT).
- The carbon nanotubes are either rectilinear or spiral and they have an average diameter of 20nm. Their value in the market is under evaluation.
- A process is proposed to exploit these findings at industrial level. The preliminary energy balance shows that a price of 0.2US\$/kg of carbon MWNT is sufficient to offset to cost of the lost energy due to the formation of the Carbon MWNT. If all other costs are added it is estimated that the break-even cost for a techno-economically sustainable process is of around 1.0US\$/kg of carbon MWNT. This price will be lowered by eventual additional revenue

coming from the selling of carbon credits associated with the CO₂ sequestration offered by the process. Thus, according to the results presented in Tables 1 and 2, for every 10US\$/tn of CO₂ sequestered the break-even selling price of the Carbon MWNT is decreased by about 0.1US\$/kg.

7. Acknowledgements

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