# Intensification of the $CO_2$ methanation process using a Packed Bed Membrane Reactor (PBMR)

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## Abstract

This work describes the results obtained in $CO_2$ methanation (Power-to-Methane, *PtM*) when operating in a new Packed Bed Membrane Reactor (PBMR). The goal is to maximize selectivities to methane ($CH_4$), using the porous membrane wall to dose one of the reagents. A Ni-Fe/γ-$Al_2O_3$ catalyst has been employed to such end.

## Introduction

In recent decades, there has been a significant development of technologies within the framework of the *Power-to-Gas* (P2G) process. This concept seeks to take advantage of surplus energy (preferably of renewable origin) for the production of a renewable *Synthetic Natural Gas* (SNG), through the *Sabatier* reaction (r.1). The methane ($CH_4$) produced can be stored or subsequently introduced into the gas network, depending on the needs of each moment [1].

$$CO_2 + 4\ H_2 \rightleftharpoons CH_4 + 2\ H_2O \qquad \text{(r.1)}$$
$$\Delta H_r^o = -165.1\ \text{kJ mol}^{-1}$$

The starting hypothesis is based on the fact that the reaction (r.1) is a series-parallel process, consisting of two stages, in which carbon monoxide (CO) is generated as an intermediate product and $CH_4$ as a final product. Thus, by distributing one of the reactants ($CO_2$ or $H_2$), the selectivities towards both products can be modified; more specifically, a distribution of $CO_2$ will lead to greater selectivity to $CH_4$ as a final product, thus increasing its production.

This hypothesis has already been confirmed in previous experimental works, using a four-inlet fixed-bed reactor [2-3], with two different catalysts. The results of this work seek to extend this research to a reactor with a porous membrane wall (PBMR), thus allowing to maximize the dosage of one of the reagents and its influence on the results.

## Experimental

The experiments have been carried out in a stainless-steel reactor, whose porous steel wall allows the distribution of a flow of gas (one of the reactants) through it. The dosed reagent is fed through a shell external to the membrane, in the same direction as the flow fed inside the catalytic bed (in parallel) or in the opposite direction (countercurrent). The fixed bed is formed by the solid catalyst (5%$^w$ Ni - 5%$^w$ Fe/γ-$Al_2O_3$), diluted with alumina (*SASOL Puralox*), occupying the entire height of the porous wall (12 cm). The particle diameter ($d_p$) is 100-200 μm. The reactants ($H_2$ and $CO_2$) were always introduced in stoichiometric proportion (4:1), in addition to two inert gases (5 %$^v$ Ar and 5 %$^v$ $N_2$) introduced as a diluent and as an internal standard, respectively. **Figure 1** shows a schematic of the reactor, as well as the five power configurations that have been analyzed in the tests.

The parameter studied in these experiments, with which different conversion values (and, therefore, selectivity) were obtained, is the contact time between the catalyst and the reactants (or space velocity, *WHSV*). To do this, maintaining a constant catalyst weight (0.2 g), the reagent flow rate ($q_0$: 504, 400, 280, 200, 100 mL (STP)/min) was modified, maintaining a temperature of 325 °C. Each flow rate was maintained for 1 hour.

The results verify that the reactor with a porous membrane wall PBMR is suitable for obtaining an improvement in the $CO_2$ methanation process. As had already been observed when operating with a four-inlet reactor, a dosage of $CO_2$ favors the formation of methane, leading to greater selectivity towards this product, than with a conventional feeding of both reactants or with an $H_2$ distribution. The results obtained are shown in **Table 1** (for constant conversion) and in **Figure 2**.

**Table 1. Selectivities to CO, $S_{CO}$, obtained at a conversion $X_{CO2}$ = 0.2, for the five reactor configurations**

| Configuration | $S_{CO}$ |
|---|---|
| Countercurrent-$CO_2$ | 0.08 |
| Parallel-$CO_2$ (estimated) | 0.10 |
| Conventional | 0.12 |
| Parallel-$H_2$ | 0.13 |
| Countercurrent-$H_2$ | 0.15 |

Additionally, it is observed that a countercurrent feeding of the dosed reagent maximizes the effect on product selectivity. Thus, maximal selectivities to CO are reached when $H_2$ is distributed in countercurrent, while methane production is most favoured when $CO_2$ (or biogas) is the gas dosed in countercurrent.

# Conclusions

This work seeks to achieve an improvement in the $CO_2$ methanation process, obtaining an increase in the selectivities of this product, through the dosage of carbon dioxide as a reagent. Operating at a temperature of 325 °C, the contact time was modified (working at five different flow rates), confirming that, for a fixed conversion value, distributing $CO_2$ leads to an increase in total methane production. Despite a decrease in conversion, the lower production of (unwanted) CO allows an advantageous configuration to be used for this reaction. This effect is accentuated by operating with the reagent distributed in countercurrent, reaching the lowest selectivities to CO, while when feeding the reagent in parallel, there is an intermediate result between a conventional feeding of both reactants and countercurrent distribution.


## Acknowledgements

Research funded by MICIU (Spanish *Ministerio de Ciencia, Innovación y Universidades*), *Agencia Estatal de Investigación* (AEI) project **PID2022-136947OB-I00** and *European Union Next Generation* **PRTR-C17.I1 Task LA4.A1**. The consolidated research group CREG (T43-23R) has received financial support from *Gobierno de Aragón* (Spain) through the European Social Fund – FEDER.


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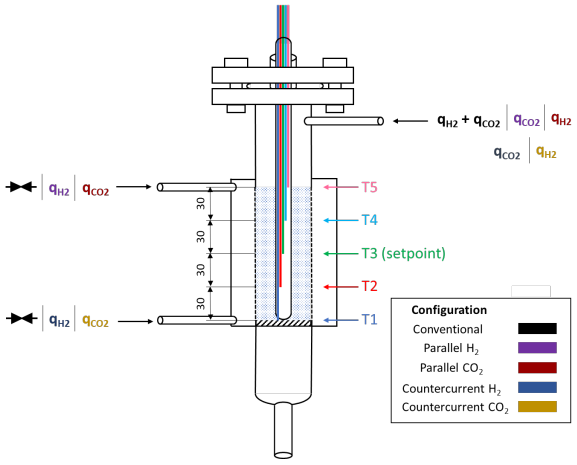


**Figure 1. Schematic of the porous membrane wall reactor (PBMR). Feeding configurations.**

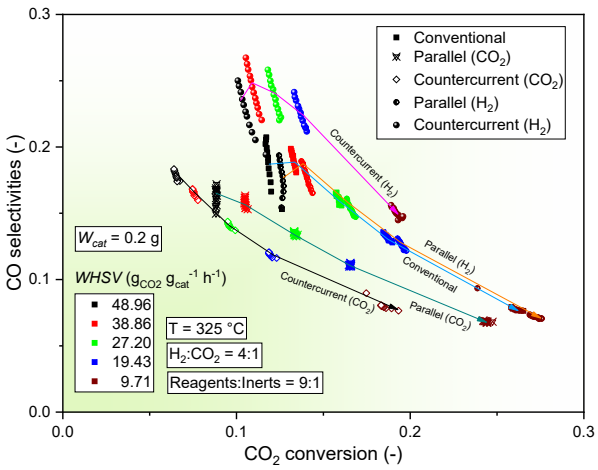


**Figure 2. Effect of reactor configuration on CO selectivities for different *WHSV* values**