# Intensification of biogas upgrading through side distribution in a Packed Bed Membrane Reactor (PBMR)

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## Abstract

This work focuses on using the *Sabatier* reaction to produce renewable methane from $CO_2$. The goal is to maximize methane generation using a new reactor configuration called *Packed Bed Membrane Reactor* (PBMR). After proving this device with pure $CO_2$, the research is now extended to using a sweetened biogas feeding.

## Introduction

Last years have seen an increased interest on production of synthetic fuels as an alternative to fossil-based ones, aiming to decrease emissions of Greenhouse Gases (GHG) into the atmosphere. Among these options, the generation of a renewable *Synthetic Natural Gas* (SNG) can be achieved using captured $CO_2$, which reacts catalytically with hydrogen through the *Sabatier* reaction (r.1).

$$CO_2 + 4\ H_2 \rightleftharpoons CH_4 + 2\ H_2O \qquad (r.1)$$

This reaction takes place in two steps, producing carbon monoxide (CO) as an (undesired) intermediate product, and $CH_4$ as the final one in a series-parallel process. Thus, one way to control reaction rates and maximize obtention of methane is to distribute carbon dioxide through the whole catalytic bed, mixing streams with different degrees of conversion of the "series" reactant [1]. This can be applied both with pure carbon dioxide streams and mixtures that contain it (such as biogas) [2].

The current research aims to test a porous wall reactor, which allows a maximal degree of dosage (*Packed Bed Membrane Reactor*, or PBMR) for the transformation of a synthetic biogas into a stream of pure methane (*biogas upgrading*). This reactor configuration has already been proven with a pure carbon dioxide stream, confirming that side distribution results in heightened selectivities to methane over CO. In addition, the $H_2$:$CO_2$ ratio was also analyzed. Since $H_2$ is more expensive and difficult to store and use, it is of interest to optimize its content in the reactor feeding. However, its defect favours CO generation, which could be solved by using a PBMR for distributed feeding.

## Experimental

The experiments were performed using a stainless-steel PBMR. This reactor (see Figure 1) contains a porous membrane wall (protected by a shell) which allows dosing of a gas flowing through one of two inlets. Depending on which inlet is used, the distributed reactant is introduced in cocurrent (↓↓) or countercurrent (↓↑) direction regarding the flow of the second reactant which feeds the reactor through the main entrance.

In order to ensure that the whole height of the membrane (12 cm) was in contact with the catalyst bed (thus avoiding any preferential flow channel), and to decrease temperature profiles, the catalyst ($5\%^w$ Ni - $5\%^w$ Fe/γ-$Al_2O_3$), was diluted in inert γ-$Al_2O_3$ (*SASOL Puralox*). Temperature and partial pressures were fixed during the experimental tests. Flowrates were modified to test different space velocities (VHSV) keeping each value for 1 hour. Total pressure was always 1 bar. A mixture composed by $CH_4$ and $CO_2$ simulated a sweetened biogas stream ($CH_4$:$CO_2$ = 7:3). In addition, Ar and $N_2$ were fed (both 5 $\%^v$), acting as dilutant and internal standard respectively. Table 1 shows the parametric values for the experiments.

A close inspection of the results (Figure 2) demonstrates that, just as it was previously observed with $CO_2$, a side distribution of biogas through the membrane increases methane selectivities over those achieved with a conventional feeding of both reactants or those with side dosing of $H_2$. The effect of distributed feeding on selectivities becomes more intense when the reactant is introduced in countercurrent (↓↑), either biogas (highest production

of methane) or $H_2$ (highest CO selectivities). Dosage in cocurrent (↓↓), meanwhile, yields intermediate values between those obtained working in countercurrent and with conventional cofeeding. These differences between behaviours are the consequence of the distributed flow entering non-homogeneously through the membrane (i.e., non-uniform introduction of the gas flow). Hence, operation with side distribution of a reactant in countercurrent results in an increased local defect, which amplifies its effect on selectivities. Studying the partial pressures of both reactants revealed that, even though selectivities behaved as expected (i.e., an excess of hydrogen increased selectivities to methane, while its defect promoted CO generation). CO formation can be reduced with distribution of biogas, as seen in Figure 3 (where CO selectivities are compared as a function of molar ratios and feeding configurations).

# Conclusions

Results of this work confirm that an enhancement of reaction performances over a conventional fixed bed regime has been achieved. Just like it was observed with $CO_2$, side distribution of biogas through the pores of the membrane leads to increased methane selectivities and establishes a *Packed Bed Membrane Reactor* (PBMR) as an advantageous configuration to carry out the methanation reaction. This improvement extends to operation with smaller $H_2$:$CO_2$ ratios, where CO selectivities are consistently kept at a low value despite defect of $H_2$ promoting formation of this undesired product.

**Table 1. Parametric operational values**

| Parameters | Value |
|---|---|
| Temperature (°C) | 325 |
| Catalyst/alumina weight (g) | 0.2/16.3 |
| $H_2$:$CO_2$ ratio (-) | 2:1 / 4:1 / 6:1 |
| Flowrates ((SATP) mL/min) | 504/400/280/200/100 |
| Feeding configurations | 5 |

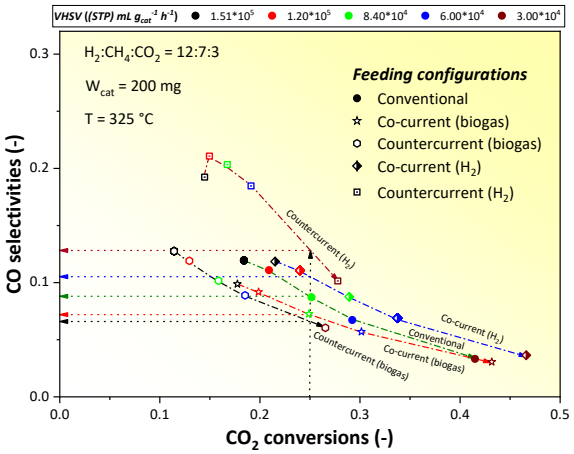


**Figure 2. Selectivities to CO versus $CO_2$ conversions, as a function of feeding configuration. $H_2$:$CH_4$:$CO_2$ = 12:7:3**

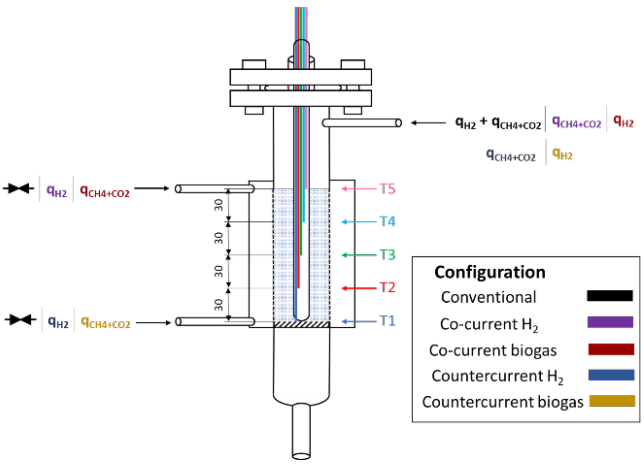


**Figure 1. Depiction of the packed bed membrane reactor (PBMR), along with the five feeding configurations**

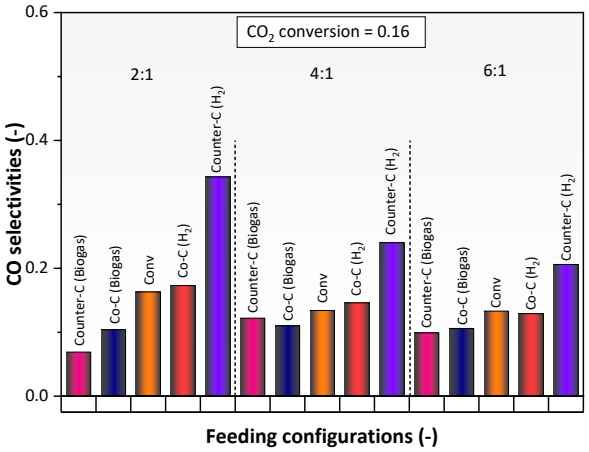


**Figure 3. Selectivities to CO versus $CO_2$ conversions, as a function of $H_2$:$CO_2$ ratios at a specific conversion (0.16)**

## REFERENCES


[1]. LEVENSPIEL, O. *Chemical Reaction Engineering, 3rd Edition*. Wiley, 1998. ISBN: 978-0-471-25424-9.

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