

Coking in a two-stages catalytic upgrading of biogas

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Highlights

- Two-staged catalytic methanation of biogas satisfies Italian grid injection requirements.
- Increase in operating pressure enhance CO₂ conversion.
- Partial interstage condensation (not total) limits carbon deposition in the second stage.

1. Introduction

Biogas is a combustible mixture of gas mainly composed of CH₄ and CO₂ and is produced from the anaerobic bacterial decomposition of organic compounds. The purified biogas can be upgraded to biomethane, a high purity methane which can be used directly as fuel or can be injected into the natural gas grid, selectively separating the CO₂ from the CH₄. A technique to avoid CO₂ venting is biogas upgrading via methanation, based on the Sabatier reaction to directly convert CO₂ to CH₄. Lot of studies [1,2] have been done on this technique, that is proved to be capable of producing biomethane satisfying the Italian natural gas grid injection requirements by means of a two-stage process with adiabatic reactors and intermediate water sequestration. This work focuses on the second stage and, particularly, on the carbon deposition and on the possibility to use steam as a tool to reduce coke deposition, which is a relevant deactivation mechanism for the commercial catalysts tested [3].

2. Methods

A scheme of the experimental plant is reported in Figure 1.

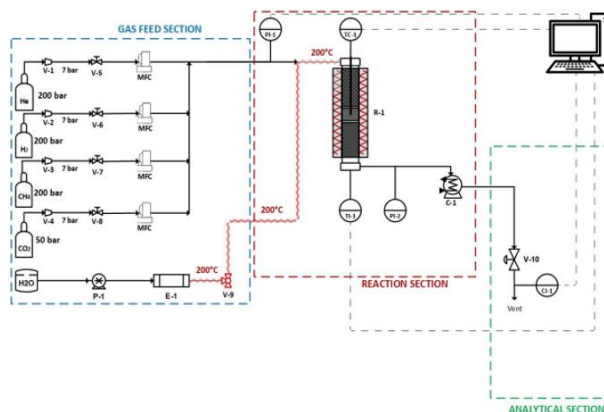


Figure 1: Scheme of the experimental set-up.

Gases are fed to the reaction section via mass flow controllers periodically calibrated, except for steam, produced from liquid water in an evaporator and flowing through heated lines. The packed bed reactor consists of an Inconel tube, filled with the commercial catalysts. Pressure and temperature are monitored and controlled by means of thermocouples, pressure transducers and a back pressure valve. After the reaction section, a condenser is required to avoid water to reach the analytical section, namely a micro gas chromatograph (μ GC). The experimental data obtained are processed with tailored scripts written in MATLAB®.

The experimental campaign is carried out according to the repetition of three different type of tests: temperature programmed reduction (TPR), to activate the fresh catalysts or reduce the active nickel after the TPO, coke-formation long duration test to verify catalyst's stability and temperature programmed

oxidation (TPO) to evaluate the quantity of solid carbon formed in the long duration test, directly related to the quantity of CO₂ produced during the TPO.

3. Results and discussion

In Figure 2 the main results are reported. In the left plot is shown how an increase in pressure enhance the Sabatier reaction, also according to equilibrium studies, thus increasing the CO₂ conversion from 69.3% to 81.7%. Also, the catalyst maintained its activity toward methanation for the whole test duration, being the variation in CO₂ conversion related to an error in the tracker composition measurement, translating in an error on the number of moles and so on the conversion's calculations, and not to any catalyst's activity loss. In the middle plot the effect of water addition to the feed (simulating a partial interstage condensation) on CO₂ conversion is shown. In both cases the pressure was equal to 6 bar. As expected from equilibrium calculations, the conversion decreases from 81.7% to 67.8%. However, in both cases the biomethane produced is in line with the Italian natural gas grid injection and the catalysts was proved to be stable for the whole test duration. From the TPOs following these two tests (right plot) the quantity of solid carbon has been evaluated. Particularly, an inlet steam molar fraction of 0.2 reduced the coking rate by 80% with respect to the test with dry inlet mixture (from 0.1022 mg_{coke}/(g_{cat}h) to 0.0224 mg_{coke}/(g_{cat}h)).

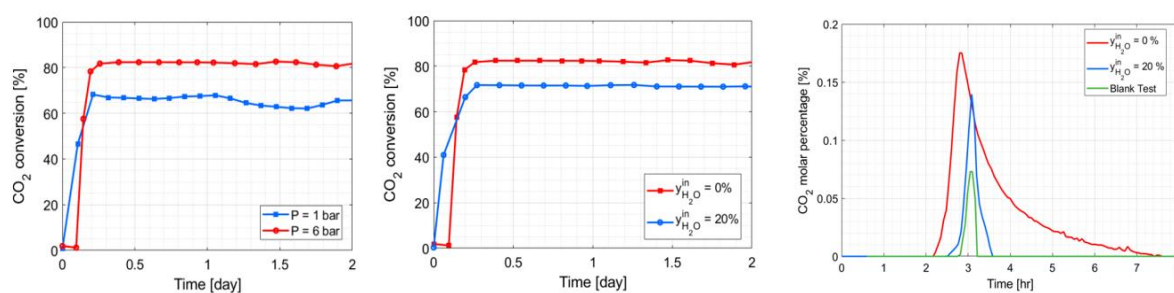


Figure 2: CO₂ conversion at 1 and 6 bar (left), CO₂ conversion at 6 bar for partial and total interstage condensation (middle), CO₂ production during TPO after tests at partial and total interstage condensation (right)

4. Conclusions

The commercial catalyst tested could maintain its activity toward methanation. This implies that the rate of solid carbon production is not high enough to lead to catalysts deactivation. This is also enlightened by the coking rate, assuming a value much lower than that obtained in industrial plants of methane cracking [4], e.g., equal to 2400 mg_{coke}/(g_{cat}h) (obtained at 500°C, with p_{H₂} = 0.2 bar and p_{CH₄} = 5 bar), against the coking rate lower than 0.11 mg_{coke}/(g_{cat}h), obtained in the experimental campaign. Furthermore, the addition of a certain quantity of water allows to reduce the coking rate by 80% (in the stress-test conditions), leading to a decrease of methane dry percentage in the product mixture of 3.3% only (from 96.4% to 93.1%), always ensuring a higher CO₂ conversion and methane enrichment than that obtained at atmospheric pressure.

References

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Keywords

Biogas catalytic methanation; Sabatier reaction; carbon deposition