COMPARATIVE ANALYSIS OF CARBON DIOXIDE METHANATION TECHNOLOGIES FOR LOW CARBON SOCIETY DEVELOPMENT

GHEORGHE LAZAROIU[1], DANA-ALEXANDRA CIUPAGEANU[1], LUCIAN MIHAESCU[2], RODICA-MANUELA GRIGORIU[1]

[1]*Power Engineering Faculty, University Politehnica of Bucharest, Splaiul Independentei 313, 060042, Romania, e-mails: glazaroiu@yahoo.com, dana_ciupageanu@yahoo.com, manuela.grigoriu.1968@gmail.com*

[2]*Mechanics and Mechatronics Faculty, University Politehnica of Bucharest, Splaiul Independentei 313, 060042, Romania, e-mail: lmihaescu@caz.mecen.pub.ro*

Conversion technologies able to transform renewable energy sources (RES) based electricity in gaseous fuels, which can be stored over long timeframes, represent a key focus point considering the low carbon society development. Thus, Power-to-Gas technologies emerge as a viable solution to mitigate the variability of RES power generation, enabling spatial and temporal balancing of production vs. demand mismatches. An additional benefit in this context is brought by the decarbonization facilities, employing polluting carbon dioxide (CO_2) emissions and RES-based electricity to produce synthetic natural gas with high methane (CH_4) concentration. The fuel obtained can be stored or injected in the gas distribution infrastructure, becoming a clean energy vector. This paper investigates the functional parameters of such technologies, aiming to comparatively analyze their suitability for further integration in hybrid and ecofriendly energy systems. Given the stability of CO_2 molecule, a catalyst must be used to overcome the methanation reaction kinetics limitations. Therefore, the required conditions (in terms of pressure and temperature) for CO_2 methanation reaction unfolding are analyzed first. Further, CO_2 conversion rate and CH_4 selectivity are investigated in order to provide a detailed comparison of available technologies in the field, addressing moreover the particularities of catalyst preparation processes. It is found that Nickel (Ni) based catalysts are performing well, achieving good performances even at atmospheric pressure and low temperatures. It is remarkable that, within a [300,500]°C temperature range, Ni-based catalysts enable a CO_2 conversion rate over 78% with a CH_4 selectivity of up to 100%. Last, integration perspectives and benefits are discussed, highlighting the crucial importance of the results presented in this paper.

Keywords: Carbon dioxide methanation; Decarbonization; Low carbon society.

INTRODUCTION

Electrification (based on renewable energy sources – RES) of energy intensive economy sectors, such as transportation, is identified as a solution to mitigate harmful emissions, therefore effective incentives must be carefully designed in this regard (Duic and Rosen, 2014). However, including progressively higher shares of strongly variable energy sources (wind, photovoltaic, wave energy, etc.) entails dealing with supply continuity issues (Eltigani and Masri, 2015). Therefore, in order to enable a slick transition towards environmentally friendly power supply also for the conventional generation, the operating traditional plants have to be upgraded. More in detail, they should comprise decarbonization technologies, facilities with improved combustion efficiency and employ alternative fuels with low carbon footprint (Balcu *et al*., 2019). Further, flexibility requirements (evaluated based on the mismatch between the energy demand and the continuous supply and the boundaries of the confidence interval limits) have to be satisfied to increase the high reliability of supply (Soares *et al*., 2017).

Technologies for the conversion of electricity into long-term gas-to-gas (P2G) energy agents play a key role in the contemporary development of low-carbon energy systems (Gallo *et al*., 2016). P2G is a viable solution for storing highly variable

https://doi.org/10.24264/icams-2020.IV.11

renewable energy in the medium and long term, thus ensuring the satisfaction of time imbalances between energy production and demand in the current uncertain context (Lazaroiu and Ciupageanu, 2019). The basic principle of P2G is represented in Figure 1 and consists in the production of a combustible gas (which can be stored or injected in the distribution network) using:

- renewable energy for obtaining hydrogen (H_2) by electrolysis;
- an additional source of carbon dioxide (CO_2) for the production of Synthetic Natural Gas (SNG), with a high content of methane (CH_4), in the methanation reaction.

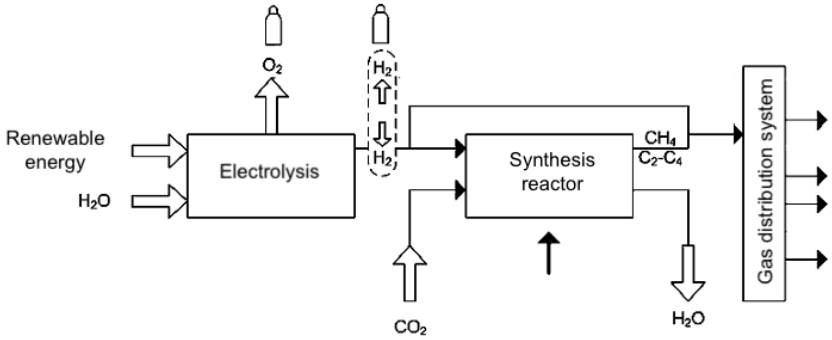

Figure 1. P2G system basic layout

It is highlighted that methanation decarbonation is technically feasible through a combination of technologies (methanation reactor, electrolyzer for H_2 production, etc.). As a result, the production of CH_4 in decarbonation processes is not currently economically competitive with conventional production technology if the use of atmospheric CO_2 is intended. A possible more accessible and implementable solution in a shorter time is by "reusing" CO_2 emitted by polluting installations. This concept falls within the field of carbon capture and use technologies, which can eliminate CO_2 emissions generated in the operation of various polluting plants (such as conventional power plants). Therefore, the functionality of the technology discussed in this paper shows a huge research potential, being yet less investigated and exploited.

CARBON DIOXIDE METHANATION TECHNOLOGY

Basic Concept

Given the stability of the CO_2 molecule, obtaining CH_4 based on it requires the use of a catalyst to overcome the kinetic limitations of the methanation reaction (1), which have high selectivity relative to CH_4 formation and be active at relatively low temperatures (Ghaib *et al*., 2016).

$$CO_2 + 4H_2 \xleftrightarrow{catalyst} CH_4 + 2H_2O \quad \Delta H = -165\ kJ/mol \tag{1}$$

It is noticeable that there are two variants through which the CO_2 methanation reaction can develop, namely the thermochemical path (showing superior performance) or electrochemical approach (Wang and Gong, 2011). More in detail, catalytic

https://doi.org/10.24264/icams-2020.IV.11

methanation of CO_2 by the Sabatier thermochemical method requires temperatures and pressures in the range, respectively, and is based on the use of metal catalysts in fixed bed or mobile reactors of specific construction. Regarding the properties of the catalyst, it is preferred to use powders, which ensure the intensification of mass and heat transfer, low pressure losses in the column and a better controllability of the reaction parameters (Castellani *et al*., 2017).

It is remarked that two important criteria in the catalyst selection and methanation tank design are CO_2 conversion rates and selectivity of CH_4 formation. Theoretically, for the thermochemical technology, the optimal thermal range, where both criteria reach high values, is in the range of low temperatures. However, the default caloric intake of the reaction can lead to increasing these temperatures (Stangeland, 2017).

In reference to the reaction temperature, it should be emphasized that values above $550℃$ should be avoided, as at such values the catalyst risks to be deactivated through sintering. On the other hand, according to le Chatelier's principle, methanation reaction development is favored at high pressures (Younas *et al*., 2016). Analyses presented in the literature show that, for temperatures in the range $[200; 500]℃$ and pressures above the value of $10\ bar$, the CO_2 conversion rate exceeds 90%.

Moreover, it was observed how highly reactive metal catalysts (Nickel - Ni or Ruthenium - Ru) causes almost exclusively the production of CH_4, while those less reactive (Palladium - Pd, Platinum - Pt, Rhodium - Rh, Molybdenum - Mo or Gold - Au) generate by-products such as carbon monoxide (CO) or methanol (CH_3OH). Therefore, Ni-based catalysts represent a viable option for CO_2 methanation, both in terms of good chemical performance and affordable costs (Wang and Gong, 2011; Stangeland, 2017).

Catalyst Preparation

The preparation of the catalyst has a very important role in the initiation and unfolding of the methanation reaction. The technique used to combine the metal with the support material affects the crystalline structure of the resulting product, its dispersion in the reactor and the catalytic activity in general (Park and McFarland, 2009). Regarding the catalyst preparation techniques, there are the following variants (Younas *et al*., 2016):

- Sol-Gel: a solid colloidal porous structure is formed from alkaline metal oxide molecules, nitrites or sulfites. Generally, for the methanation catalytic reaction, this metal catalyst is generated by combining metal salts with the base metal.
- Synthesis of micro-emulsions produces catalysts with large contact surface and very good dispersion of the metal phase, which improves the methanation reaction.
- Capillary impregnation: used to obtain heterogeneous catalysts. In principle, the active metal is dissolved in an aqueous or organic solution, with which the support material is impregnated (by absorption).
- Double impregnation: involves two steps, namely impregnation of the support (inorganic) with an organic reagent and, after drying, impregnation with an ionic solution of the active metal.
- Precipitation / deposition.

The following evaluations are conducted to compare the optimal conditions under which a Ni-based catalyst (in particular Catalyst 1 - Ni/Al_2O_3 and Catalyst 2 - Ni/Al hydrotalcite) allows to obtain the maximum performance in the catalytic reaction of

https://doi.org/10.24264/icams-2020.IV.11

CO_2 methanation at atmospheric pressure in a fixed bed reactor. For the first option, the support is obtained by the Sol-Gel method and subsequently impregnated sequentially. For the second solution considered, the catalyst is obtained by co-precipitation in an alkaline solution. According to Figure *2*, it is highlighted that:

- for Ni/Al_2O_3 (Catalyst 1), the optimal temperature range for which the CO_2 conversion rate reaches the maximum value (78%) is between;
- for Ni/Al hydrotalcite (Catalyst 2), the CO_2 conversion rate increases linearly with temperature, being higher than 90% over the whole temperature range taken into account.

It is remarked that both solutions reach 100% selectivity for CH_4 formation.

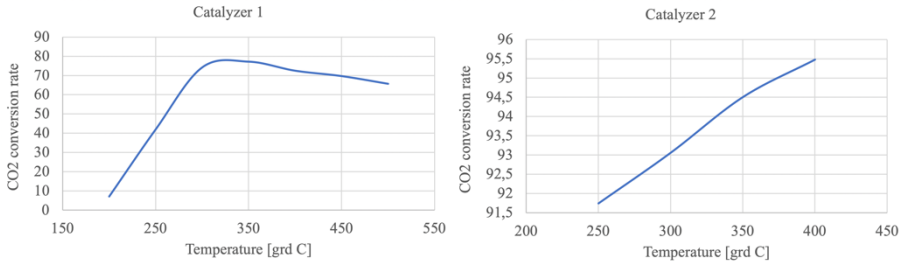

Figure 2. Reaction conditions comparison

INTEGRATION PERSPECTIVES IN ENERGY SYSTEMS

In addition, the advantages of integrating such a facility into more complex architectures that include an integrative sectoral approach are also discussed. One of the advantages of storing energy in the form of CH_4 (compared to storing it in the form of H_2) is that there are no quantitative (but only qualitative) restrictions on CH_4 delivered to the gas distribution network. If the SNG obtained in the methanation process does not have a sufficiently high CH_4 content, then further purification must be carried out for use in energy or transport applications (Blanco *et al*., 2018). The disadvantage is the higher investment in equipment. In order to design a technically and economically advantageous solution, the current or feasible possibilities must be weighed in the near future for the use of CH_4 and H_2 (Salomone *et al*., 2018).

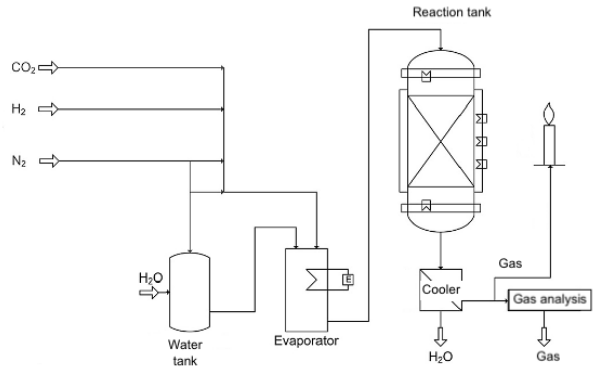

Figure 3. Integration of methanation facility

https://doi.org/10.24264/icams-2020.IV.11

A possible integration solution of CO_2 methanation facilities in the current energy framework is by connecting them to the exhaust of diesel generators, employed as UPS (Uninterruptible Power Supply). It is feasible to partially supply the diesel group fuel flow (up to 80% (Balcu *et al*., 2019)) by feeding the flue gas at the exhaust of a diesel group to the methanation unit. The amount of CH_4 that can be obtained represent a cleaner alternative to diesel fuel (based on equations (2) and (3)).

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + Q_{methane} \quad (2)$$

$$C_{16}H_{34} + \frac{49}{2}O_2 \rightarrow 16CO_2 + 17H_2O + Q_{diesel} \quad (3)$$

As a consequence of different heating values, it is demonstrated in Balcu *et al*. (2019) that the fuel flow can be reduced with approximately 16%, while the emissions are brought down by up to 27%.

CONCLUSIONS

In a framework highly oriented towards innovation and new technology development, intensive research is necessary to enable market penetration and wide diffusion of cutting-edge solutions. Improved and highly efficient technologies are still needed to achieve acceptable levels of emissions while ensuring mitigation of RES related effects on power systems behavior. In high-penetration renewable energy systems, the variability of electricity generation sources must be mitigated, in order to enable their optimal exploitation. For this purpose, they have to comprise flexibility resources (such as storage devices) additional fully controllable generating units (diesel groups, for instance) and, sometimes, flexible demand. In this environmentally restricted and increasingly uncertain power generation context, the paper addresses the selection of catalysts for a methanation tank possibly coupled to a diesel generator, considering a further innovative and integrative approach within hybrid energy systems. It is highlighted the need to establish a compromise solution, affordable and able to ensure high values of CO_2 conversion rate and selectivity in the formation of CH_4, under conditions of pressure and temperature that involve low energy consumption.

Acknowledgments

This work was supported by a grant of the Romanian Ministry of Research and Innovation, CCCDI-UEFISCDI, project number PN-III-P2-2.1-PED- 2019-2350, within PNCDI III, contract number 322PED/2020.

REFERENCES

Balcu, I. *et al*. (2019), "Decarbonization of Low Power Applications through Methanation Facilities Integration," in: *IEEE PES Innovative Smart Grid Technologies Europe – ISGT-Europe*, Presented, https://doi.org/10.1109/ISGTEurope.2019.8905506.

Blanco, H., Nijs, W., Ruf, J., and Faaij, A. (2018), "Potential of Power-to-Methane in the EU energy transition to a low carbon system using cost optimization", *Appl. Energy*, 232, 323–340, https://doi.org/10.1016/j.apenergy.2018.08.027.

Castellani, B. *et al*. (2017), "Experimental investigation on CO_2 methanation process for solar energy storage compared to CO_2-based methanol synthesis", *Energies*, 10(7), 1–13, https://doi.org/10.3390/en10070855.

Duić, N. and Rosen, M.A. (2014), "Sustainable development of energy systems", *Energy Convers. Manag.*, 87, 1057–1062, https://doi.org/10.1016/j.enconman.2014.08.046.

Eltigani, D. and Masri, S. (2015), "Challenges of integrating renewable energy sources to smart grids: A

https://doi.org/10.24264/icams-2020.IV.11

review", *Renew. Sustain. Energy Rev.*, 52, 770–780, https://doi.org/10.1016/j.rser.2015.07.140.

Gallo, A.B., Simões-Moreira, J.R., Costa, H.K.M., Santos, M.M., and Moutinho dos Santos, E. (2016), "Energy storage in the energy transition context: A technology review", *Renewable and Sustainable Energy Reviews*, 65, 800-822, https://doi.org/10.1016/j.rser.2016.07.028.

Ghaib, K., Nitz, K., and Ben-Fares, F.-Z. (2016), "Chemical Methanation of CO_2: A Review", *ChemBioEng Rev.*, 3(6), 266–275, https://doi.org/10.1002/cben.201600022.

Lazaroiu, G. and Ciupageanu, D. (2019), "Multi-criteria decision making in sustainable renewable energy systems", in *19th International Multidisciplinary Scientific Geoconference SGEM2019*, 19(4.1), 569–576, https://doi.org/10.5593/sgem2019/4.1/S17.042.

Park, J. and McFarland, E. (2009), "A highly dispersed Pd-Mg/SiO_2 catalyst active for methanation of CO_2", *J. Catal.*, 266(1), 92–97, https://doi.org/10.1016/j.jcat.2009.05.018.

Salomone, F., Giglio, E., Ferrero, D., Santarelli, M., Pirone, R., and Bensaid, S. (2018), "Techno-economic modelling of a Power-to-Gas system based on SOEC electrolysis and CO_2 methanation in a RES-based electric grid", *Chem. Eng. J.*, 1–20, https://doi.org/10.1016/j.cej.2018.10.170.

Soares, J., Fotouhi Ghazvini, M.A., Borges, N., and Vale, Z. (2017), "A stochastic model for energy resources management considering demand response in smart grids", *Electr. Power Syst. Res.*, 143, 599–610, https://doi.org/10.1016/j.epsr.2016.10.056.

Stangeland, K., Kalai, D., Li, H. and Yu, Z. (2017), "CO_2 Methanation: The Effect of Catalysts and Reaction Conditions", *Energy Procedia*, 105(1876), 2022–2027, https://doi.org/10.1016/j.egypro.2017.03.577.

Wang, W. and Gong, J. (2011), "Methanation of carbon dioxide: An overview", *Front. Chem. Eng. China*, 5(1), 2–10, https://doi.org/10.1007/s11705-010-0528-3.

Younas, M., Loong Kong, L., Bashir, M.J.K., Nadeem, H., Shehzad, A., and Sethupathi, S. (2016), "Recent Advancements, Fundamental Challenges, and Opportunities in Catalytic Methanation of CO_2", *Energy and Fuels*, 30(11), 8815–8831, https://doi.org/10.1021/acs.energyfuels.6b01723.

https://doi.org/10.24264/icams-2020.IV.11