Analysis of innovative decarbonation technologies by methanation

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Abstract: In the development process of Romania, the energy sector for 2030 contributes essentially through its influence on the quality of life, the environment, the competitiveness of the economy, as well as the climate [1]. Thus, the energy sector from Romania must become more economically efficient, less polluting, and more technologically advanced. This paper presents the analysis of innovative methanation decarbonation technologies, the following aspects were pursued: methanisation, the reactions involved and the importance of the methanisation process, methanisation technologies and methane use, decarbonisation through methanisation, the importance of catalysts in methanation processes, decarbonisation with Carbon Capture Storage (CCS), catalyst enabled processes. Behind modern methanation decarbonization technologies is a history of over 100 years based on research and development [2]. At present, methanization is in the attention of scientists, industry, and energy companies, because: fossil fuels are a finite resource that will soon be exhausted; the energy system is constantly changing, and renewable energies are playing an increasingly important role in it; increasing levels of CO2 in the atmosphere contributes to global climate change.

1. Introduction

With the publication of the Energy Union Strategy (under the Paris Agreement on the supply of clean energy throughout the European Union), the EU has taken on an important role in combating climate change. In terms of energy and climate in 2030: reduction of domestic greenhouse gas emissions by at least 40% by 2030, compared to 1990; renewable energy consumption of 32% in 2030; energy efficiency improvement by 32.5% in 2030; interconnection of the electricity market at a level of 15% by 2030 [1].

In the process of Romania's development, the energy sector for 2030 contributes essentially through its influence on the quality of life, the environment, the competitiveness of the economy, as well as the climate (figure 1). Thus, the energy sector in Romania must become more economically efficient, less polluting, and more technologically advanced.

Romania will largely replace electricity production capacities by 2030 with new ones, due to the fact that they are economically inefficient and ecologically inadequate based on advanced technologies [2].
Solar energy has seen phenomenal growth in recent years due to both technological improvements that have led to cost reductions and government policies that support the development and use of renewable energy [3].

Solar energy has undergone an impressive technological change. While early solar technologies consist of small-scale photovoltaic (PV) cells, recent technologies are concentrated solar energy (CSP) and also large-scale photovoltaic systems that feed into electricity grids.

Figure 1. Global energy demand for the period 1990-2030.

2. Methods
In this paper, an experimental study of the methanation process was performed with an installation that aims to determine the optimal operation and find suitable conditions for carbon dioxide methanation catalysts. The methanation test facility was designed and commissioned to investigate the catalytic methanation of carbon dioxide and hydrogen. The process flow chart is shown in the following figure 2.

Figure 2. Process flow chart.
Due to the extremely exothermic nature of the methanation reaction, the design of the reactor is crucial to have thermal control over the system. There are basically two types of state-of-the-art reactors that can be used for this process: two-phase fixed bed reactors and reactors with fluidized bed. Regardless of the choice of reactor, the heat generated by the methanation reaction must be continuously removed from the reactor.

For carbon dioxide methanation an increase in the molar gas fraction of methane gas of about 1% in the product gas induces a temperature rise of about 60 K.

The fluidized bed reactor is presented by a large transfer of mass and heat due to the good mixing of gases and catalyst particles in the fluidized bed which results in an almost isothermal process [4]. To remove the reaction heat, a heat exchanger is installed inside the reactor. However, fluidization leads to a shredding of the catalyst due to high mechanical stress. Moreover, fluidized bed reactors are limited by the fluidization rate which restricts their flexibility.

Fixed bed reactor- Water is introduced into an evaporator to form water vapor. The reaction gases are also introduced into this evaporator. The mixture of CO2 and H2 and water vapor is introduced into the heated fixed bed reactor. Heating as well as proper insulation of the reactor was necessary to minimize heat loss and to achieve quasi-adiabatic process conditions.

Upon leaving the reactor, the gas was cooled to condense the water contained in the reaction mixture. Pressure valves were installed on the reactor to control the pressure in the reactor. The composition of the gas produced was analyzed after leaving the reactor.

High reaction temperature and sensitive catalysts are the main reasons why methanization is considered a difficult process to control, with a history based on research and technological development [5].

A good catalyst, in addition to the property of dissociation of water with the formation of oxygen and hydroxide - reactive intermediates adsorbed on the surface of the catalyst - should be able and break the C-C bond, especially in the case of opening aromatic rings. Adsorbed reactive intermediates can combine with fragments of organic compounds and form CO and CO2, while the release of adsorbed hydrogen atoms leads to the formation of hydrogen molecules. In addition, a suitable gasification catalyst must favor the steady-state development of the water-gas change reaction and the hydrogenation of CO and CO2 with CH4 formation [6, 7].

The temperature released in the reaction can lead to the sintering of the metal as a catalyst, which in turn leads to a decrease in its total surface area and to a decrease in its activity. Catalyst deactivation can also occur due to coke deposits, a situation in which the metal surface is blocked by carbon accumulation [8, 9]. In order to avoid these problems, the aim is to identify an efficient catalyst for the methanation reaction, which has high thermal stability and resistance to coke deposits.

According to Bartholomew, deactivating Ni-based methanization catalysts can be mechanical, chemical and thermal.

We recall three mechanical methods (fouling, wear and crushing), two chemical methods (poisoning and vapor-solid reactions) and a thermal method (thermal degradation), used to deactivate catalysts.

3. Experimental researches

3.1. The reagent mechanism

• Equilibrium concentrations of carbon oxides 10 ppm
• CO inhibits CO2 methane.

This reaction takes place according to a two-stage mechanism. In a first step, CO2 and H2 are converted to CO and steam by the reaction (equation (1)):

$$CO_2 + H_2 \rightarrow CO + H_2 O$$ (1)

In the second stage, CH4 is synthesized from CO and H2 (equation (2)):

$$CO + 3H_2 \rightarrow CH_4 + H_2 O$$ (2)

• Very high intrinsic reaction rates.
3.2 Methanation reactions and operating conditions

- CO2 methanation reaction is an exothermic catalytic reaction that usually takes place at temperatures between 150°C and 550°C (equation (3)).

\[
\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} + 165 \text{kJ/mol}
\] (3)

- The reactions are extremely exothermic:
  - 76°C for every 1% CO converted;
  - 66°C for every 1% CO2 converted.
- Typical inlet temperatures: 15-40°C;
- Carbon dioxide concentration at the inlet: 0.1-1.0% vol.

3.3 Pre-reduced Methanation Catalyst

- Catalyst first reduced, then partially stabilized:
  - Faster plant start-up;
  - Higher catalyst activity.
- Reduction taken place under controlled conditions
  - Higher Ni surface area;
- Lower inlet temperatures possible.
  - Minimum inlet temperature 170°C (338°F);
- Catalyst is ready to go.

4. Results and interpretations

The Ni-based catalyst was physico-chemically analyzed before and after use by the following analysis techniques: X-ray diffractometer (using a PANalytical diffractometer, with Cu-Kradiations (\(\lambda = 0.15406 \text{ nm}\)) in a 2θ range from 20° to 80°, and a scan rate of 2°/min), scanning electron microscopy and Edx (Scanning Electron Microscope Inspect S) and atomic force microscopy (Nanosurf® EasyScan 2 Advanced Research Model).

4.1. Analyzes for Ni-based catalyst before use

4.1.1. X-ray diffraction - The structural analysis of the Ni-based catalyst, before use, is shown in figure 3. The diffraction spectrum was refined with the X Pert HighScore Plus program, using JCPDS card no.: 00-001-1260. The diffraction peaks for were indexed to the cubic phase, Fm-3mspace group, with lattice parameters a = b = c = 3.5175 Å, and a unit cell volume of V = 43.52 Å3.

![Figure 3. The structural analysis of the Ni-based catalyst.](image-url)
4.1.2. Scanning electron microscopy/Edx - Electron microscopy images and semi-quantitative analysis by Edx are shown in figure 4.

![SEM images](image1)

![EDX spectrum](image2)

**Figure 4.** SEM images (a, b) and EDX spectrum (Insert quantification) (c) of the Ni-based catalyst.

From these images it can be seen that the particles are strongly agglomerated in asymmetric formations, and the semiquantitative analysis showed that the predominant element is Ni (66.49 Wt%).

4.1.3. Atomic force microscopy - Figure 5 present the 2D and 3D topography for the Ni-based catalyst. The dimensions of the particles that are present on the surface were determined by using the *Nanosurf EasyScan 2* software (figure 6).
Figure 5. 2D and 3D AFM surface images of the Ni-based catalyst.

Figure 6. The particle size distribution for the Ni-based catalyst.
The surface roughness - the average roughness (S_a) and the mean square root roughness (S_q) were calculated also from AFM analysis data. The investigated/measured surface had an area of 5.305 pm² (figure 6).

4.2. Analyzes for Ni-based catalyst after use X-ray diffraction
Figure 7 shows the X-ray diffraction spectrum for the Ni-based catalyst after use. The diffraction spectrum was refined with the X Pert High Score Plus program, using JCPDS card no.: 01-087-0712. The diffraction peaks for were indexed to the cubic phase, Fm-3m space group, with lattice parameters a = b = c = 3.5238Å, and a unit cell volume of V = 43,76Å³.

![X-ray diffraction spectrum](image)

**Figure 7.** X-ray diffraction spectrum for the Ni-based catalyst after use.

4.2.1. Scanning electron microscopy/Edx - Figure 8 shows the surface morphology for the Ni-based catalyst after use. Thus, at the higher magnification (6000X) it can be seen that the particles are very agglomerated in asymmetric formations.

![Surface morphology](image)

**Figure 8.** The surface morphology for the Ni-based catalyst after use.

4.2.2. Semi-quantitative analysis by Edx - The elemental analysis and quantification for the studied material is presented in figure 9. As can be seen from the EDAX spectrum, the predominant element is Ni, in mass percentages of 84.01%.
4.2.3. Atomic force microscopy - 2D and 3D topography for the Ni-based catalyst after use are presented in Figure 10. Although atomic force microscopy analysis was performed at the same scale of 2.29 μm x 2.29 μm for the Ni-based catalyst before and after use, it can be seen that in the case of the Ni-based catalyst used the particles are much smaller.

Figure 9. The elemental analysis and quantification for the Ni-based catalyst after use.

Figure 10. 2 D and 3D AFM surface images for the Ni-based catalyst after use.
The surface roughness - the average roughness ($S_a$) and the mean square root roughness ($S_q$) were calculated also (figure 11), and the investigated/measured surface had an area of 5.305 $\text{pm}^2$ (figure 11).

![Graph showing particle size distribution](image)

**Figure 11.** The particle size distribution for the Ni-based catalyst after use.

The figure 12 below shows the amount of $\text{H}_2$ during the methanation reaction.

![Graph showing H2 amount during methanation](image)

**Figure 12.** The amount of $\text{H}_2$ during the methanation reaction.

During the methanation reaction it can be observed that for a temperature variation of up to 10 $^\circ\text{C}$ the percentage of $\text{H}_2$ increases up to 0.20%, after which it has a stationary level of up to 0.70%. For slightly sensitive temperatures above 10 $^\circ\text{C}$, the hydrogen variation is up to 0.85%, after which it decreases.

The figure 13 below shows the resulting amount of methane.
Figure 13. The resulting amount of methane.

As can be seen from the graph, the percentage of CH₄ increases in proportion to temperature. The maximum value for CH₄ is 2% for a temperature of 80°C.

5. Conclusions
From a global viewpoint, research in this field encompasses the following:
- To counter global warming, the reaction between hydrogen and CO₂ has attracted attention.
- This method is effective for CO₂ reduction measures.
- Carbon dioxide methanation requires a catalyst to be active at relatively low temperatures and selective towards methane.
- Nickel based catalysts are most widely investigated, and commercial catalysts are typically nickel on alumina support.
- Superficial gas velocity - The increase of the inlet gas flow rate enhances the productivity of the reactor for fast reactions but restricts conversion for slower reactions that requires more contact time, which suggests that the flow rate can be optimized for specific reactions.

6. References
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