THE HYDROGEN - CARBON DIOXIDE BINOMIAL, A POSSIBLE NEW ENERGY VECTOR

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The article aims to highlight the conceptual aspects of a new innovation of the use of hydrogen versus carbon dioxide. The challenge of using the hydrogen-carbon dioxide binomial through energy conversion processes as a low-carbon technology, contributing significantly to the achievement of decarbonization goals. The use of hydrogen in the process of reducing carbon dioxide is a topic increasingly addressed in the literature as an innovative depollution process for classical plants, very important in terms of the transition to climate neutrality. The presented model represents an innovative and energy-efficient solution that responds to the problems of carbon capture and storage.

Keywords: methanization, hydrogen, decarbonization, carbon capture and storage

1. Introduction

In the development of low-carbon energy, today special concerns are given for the subsequent capture and storage of the CO_2 component. Numerous technologies have been developed for this purpose, the technical and scientific criteria being followed by financial analyzes.

The present paper brings a new ecological analysis on the CO_2 component, by transforming it with the help of hydrogenation under combustion, so that carbon dioxide together with hydrogen becomes a possible energy vector.

The recent technical advances with economic positive reflection on the production of methanol by the reaction CO_2 with H_2 have opened a new path in its use. The paper presents an original model by applying the methanization process to the combustion products resulted from an energy installation materialized by transforming the component CO_2 and CH_4.

This perspective of using methanation has not been addressed in the literature.

The appearance of methane in the flue gases requires a second combustion, with a cumulative final result with a significant reduction in the final emission of CO_2.

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All this energy chain developed in the paper is an innovative model developed by the authors.

Simple decarbonization technology includes the capture and storage chain, very technologically complicated and very expensive technology, Fig. 1. The use of hydrogenation of carbon dioxide with the production of methane and methanol respectively leads to a new conception of the final route for $\boldsymbol{CO_2}$. In the proposed new model, carbon dioxide is recirculated, finally eliminating its difficult and expensive storage.

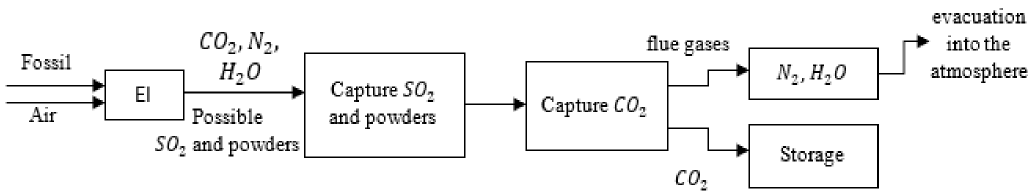

Fig. 1. The decarbonized fossil-gas fuel circuit
EI – energy installation

Fig. 2 shows the coupling in an energy installation (EI) and a hydrogenation plant (HP) to achieve the chain with H_2 energy vector.

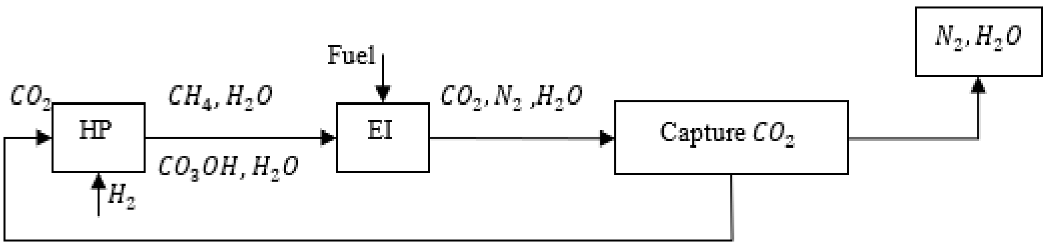

Fig. 2. Conversion of carbon dioxide into an energy vector by hydrogenation

Hydrogenation includes two technologies:

- methanization, with product, CH_4 and H_2O
- methanolization, with product, CH_3OH and H_2O

Thus, the following possibilities of using hydrogen in order to reduce carbon dioxide in combustion gases are distinguished: [1] [2]

- methanization of carbon dioxide from flue gases by synthetic reaction:

$$CO_2 + 4H_2 = CH_4 + 2H_2O \tag{1}$$

- production of methanol from carbon dioxide by synthetic reaction:

$$3H_2 + 3CO_2 = CH_3OH + H_2O \tag{2}$$

Both fuels produced by methanization lead to the imposition of carbon dioxide capture and its reuse in a circular energy in the production of initial fuels (the capture of CO_2 by CaO and $Ca(OH)_2$ allows a thermal extraction for CO_2).

- hydrogen combustion with air:

$$H_2 + 0{,}5O_2 = H_2O \quad (3)$$

2. Process analysis for reducing CO_2 from flue gases

2.1. Methanization technology for conversion CO_2 to CH_4

The capture of $\boldsymbol{CO_2}$ in the form of $\boldsymbol{CH_4}$ involves the use of a reactor (methanizer), a chemical reaction involving hydrogen. The chemical reaction of methanation present by reaction (1), involves a certain level of temperature and pressure and is under the influence of a catalyst. Mathematical modeling must respond to the importance of parallel chemical reactions (which include methanization under the CO product and counter-reaction of water on the gas, but also on the reaction speed, which involves the control of the reaction time) **[3]**, **[4]**, **[5]**, **[6]**.

The stages of the final reaction include the phases:

$$CO_2 + H_2 = CO + H_2O \quad (4)$$

Exothermic reaction ($\Delta H = 41\ kJ/mol$)

$$CO + 3H_2 = CH_4 + H_2O \quad (5)$$

Endothermal reaction ($\Delta H = -206\ kJ/mol$).

The presence of the endothermic reaction requires heating the reactor to the temperature level optimal for the catalyst used.

The best results were shown by those who used a nickel/alumina catalyst, such as the MKM-4A catalyst, for the temperature range 220-250 °C.

The mathematical models presented in the research stages of the work **[7]** from 2022 included the Langmuir-Hinshelwood mechanism. In this research, the aim was to determine the optimal pressure for the methanization reaction in an environment with a low concentration of $\boldsymbol{CO_2}$, including the use of pressure at 1 bar, the existing pressure in the flue gases discharged from the energy combustion plants. On hydrogen consumption, the resulting optimal ratio was 3-4 compared to $\boldsymbol{CO_2}$.

The material balance of anhydrous flue gases obtained from an energy installation (EI) operating with natural gas fuel, after hydrogen methanization, is shown in Fig. 3**.**

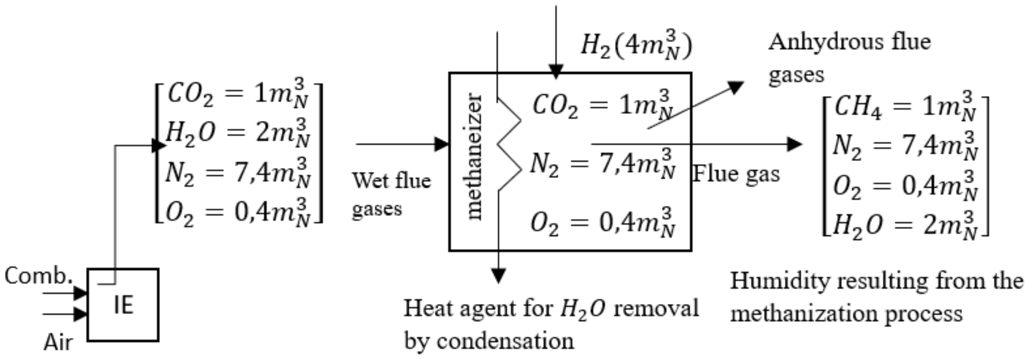

Fig. 3. Material balance of the methanization process

The presence of the combustible component $\boldsymbol{CH_4}$ in the flue gases at the outlet of the methaneizer requires an energy reuse, especially since methane cannot be discharged into the atmosphere.

As a result, the flue gases produced after the methaneizer are to be burned in a new technological installation $\mathbf{EI_2}$.

Compared to the simple energy installation, without the insertion of the methaneizer, the final $\boldsymbol{CO_2}$ emissions are 29% lower. The overall efficiency of the energy cycle directly depends on the efficiency value of the methaneizer. It can be defined by the ratio between the volume of $\boldsymbol{CO_2}$ at the outlet, $\boldsymbol{V^e_{CO_2}}$, compared to the one at the inlet $\boldsymbol{V^i_{CO_2}}$: **[8]**, **[9]**, **[10]**.

$$\eta = \frac{V^e_{CO_2}}{V^i_{CO_2}} \tag{6}$$

This efficiency of methanization defined on energy criteria is different from that of the efficiency of the methanization process X_{CO_2}, a criterion that has the expression:

$$X_{CO_2} = \frac{V^i_{CO_2} - V^e_{CO_2}}{V^i_{CO_2}} \times 100[\%] \tag{7}$$

The theoretical values of the previously presented methanization will be dependent on the constitutive characteristics of the flue gases.

The efficiency of the methanizer, like the other efficiency criteria for flue gases by volume V_g, depend on the value of the concentration of carbon dioxide, as well as on its relation to each gas in the flue gases.

$$\eta_M = f\left(\frac{V_{CO_2}}{V_g}, \frac{V_{CO_2}}{V_{N_2}}, \frac{V_{H_2O}}{V_{N_2}}, \frac{V_{O_2}}{V_{N_2}}\right) \tag{8}$$

Research in the literature included low percentages of waste gases in the flue gases subject to the methanization operation, within the limits: [3], [4].

$$\frac{V_{O_2}}{V_{N_2}} = 0,1 - 0,2$$
$$\frac{V_{H_2O}}{V_{N_2}} = 0,15 - 0,22 \quad (9)$$

The variation of the efficiency of the methanizer under the influence of waste gases, varies within the limits of 3-10% more accentuated for O_2 than for H_2O. Fig. 4 shows the efficiency of methanation depending on the thermodynamic working conditions and the concentration of waste gases. The data shown in Fig. 4 demonstrate a high level of methanization, even in the presence of H_2O and O_2 waste gases which have a negative overall effect.

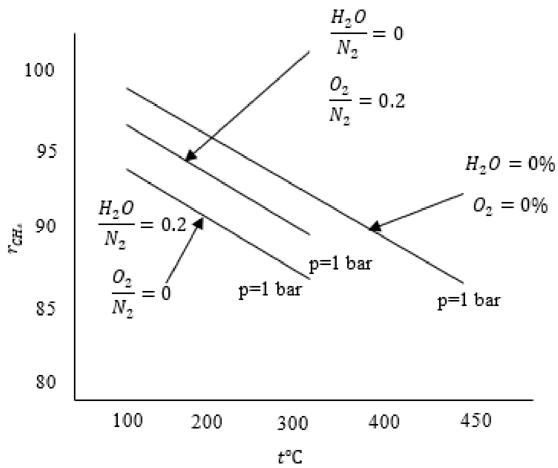

Fig. 4. Variation in the efficiency of methanization r_{CH_4} depending on the composition of the flue gas

In order to test the methanization process, an experimental pilot installation was performed during the research *[7]*.

Fig. 5 shows the scheme of the experimental methanizer installation at the National Research and Development Institute for Electrochemistry and Condensed Materials from Timișoara, used by the joint team from the Politehnica University of Bucharest and ICDE Timișoara.

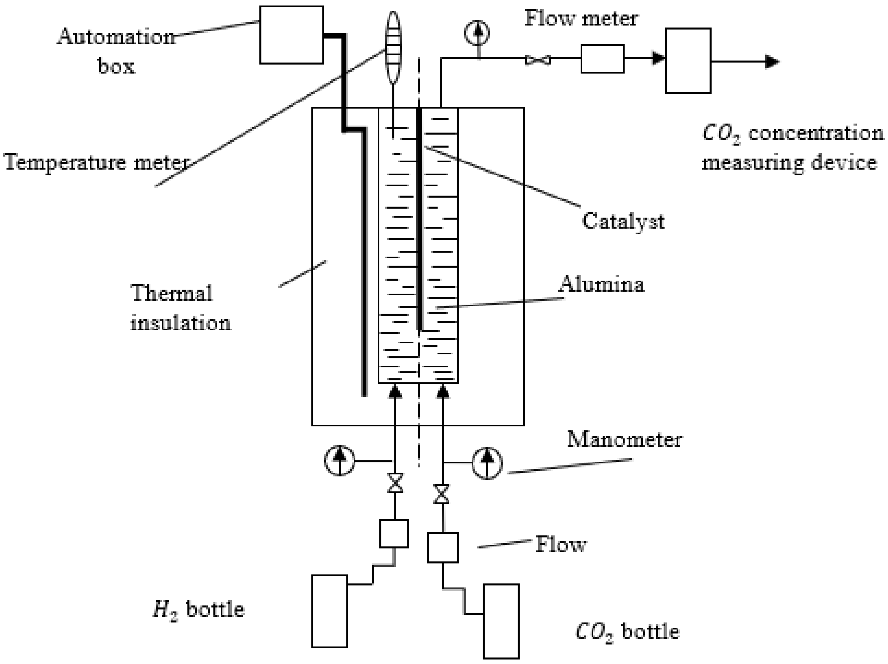

Fig. 5. Pilot metanization installation made during research

For the decarbonization of the flue gases, a continuous operation of the installation is required, a situation that imposes the following conditions:

- Heating the installation to a temperature of $60 - 120$°C using electrical resistance.
- Evacuation of air from the reactor using carbon dioxide (the operation will end when the concentration of CO_2 will be over 99%).
- Maintaining the flow CO_2 in the reactor
- Introduction of hydrogen in the flow ratio of 4:1 compared to CO_2,
- Compliance with the mass speed imposed by the time required for the methanization reaction by an adequate pressure in the reactor
- Reactor operating temperature measurement
- Concrete measurement of the reaction CO_2 at the outlet of the plant and determination the methanization of the methanization grade criterion X_{CO_2}.

Preliminary samples showed a methanization efficiency within the limits of $\eta_M = 0,72 - 0,82$.

2.2. Energy use of methanol

Residential heating in areas without natural gas supply, instead of liquid hydrocarbons or wood can use methanol in a circular energy system.

Internal combustion engines that using methanol can also be used in terms of energy installations, including cogeneration mode. Carbon dioxide capture can be introduced at these installations, while maintaining the energy vector character for CO_2.

With regard to the use of methanol in transport, reference should also be made to the production of methanol by fermentation, with a priority consideration of its price. When referring to the use of methanol in internal combustion engines, agriculture using machinery equipped with such facilities must also be considered.

2.3. Technology of injecting hydrogen into natural gas

The emission production CO_2 from the combustion of hydrogen mixed with methane is directly proportional to the volumetric participation X of hydrogen in methane.

The emission of CO_2 complies with the following quantities [11]:

$$1m_N^3CH_4 \rightarrow 1m_N^3CO_2$$
$$xm_N^3H_2 + (1-x)m_N^3CH_4 \rightarrow (1-x)m_N^3CO_2 \quad (10)$$

Hydrogen has the lower and upper limit of flammability in air of about 4% and 74% respectively, unlike methane which has the upper limit of 17%. This aspect, together with that of the combustion rate (of range of flame front for hydrogen), leads to its characterization as a particularly dangerous and difficult to use fuel.

At the current technical stage, it is considered that hydrogen can be mixed with methane in proportions of up to 15-20%, by injection into natural gas pipelines, without technically and economically significant investments. European standard EN 16726/2015 specifies that a recommendation for the limit value for the injection of hydrogen into the natural gas network is not yet provided.

It is established that by increasing the proportion of hydrogen in the natural gas network, a number of major changes in the assembly of installations will occur as necessary. These will include (polyethylene or steel pipes), compressors, safety features and automatisms, and the cost of investments will be significantly high.

The technical problems are complemented by the financial ones, since the price of hydrogen (especially the green one) will differ significantly from that of natural gas. Environmental taxes through pollution CO_2 will also be under a strong transforming factor.

3. Conclusions

The paper analyzed the possibility of using the binomial hydrogen– carbon dioxide for the formation of methane and methanol products, so that carbon dioxide

no longer represents just a waste that is difficult to capture, and store with difficult and very expensive technologies. As a result, after its capture, carbon dioxide will become an energy vector, disappearing the storage phase with all technical, ecological and economic problems.
This recirculation model for CO_2 captured, represents an original concept, developed primarily by the authors. An important theoretical and experimental step, carried out by the authors, included the metanization of flue gases with the aim of transforming the component CO_2 in CH_4. The next resulting step involved a second combustion step for CH_4 of the flue gases, with a significant final reduction in CO_2 emissions.

These energy models for a circular energy are novelties in the mathematical-experimental testing phases.
In order to reduce the emission of CO_2 during the combustion of methane, the specific problems of possible injection of hydrogen into methane were also analyzed, obtaining a fuel mixture with a lower emission of CO_2, proportional to the grade of blending.
The technology is still in the first testing phase worldwide and in Europe.
The hydrogenation of carbon dioxide in order to methanize flue gases is an effective decarbonation solution. The results obtained during the methanation of carbon dioxide in a pilot methanizer were presented. The results obtained recommending the technology for also for capturing the CO_2 component from flue gases. However, the production of methane following the methanization of carbon dioxide requires a combustion of cascading flue gases. This original model was developed by the authors [7].

The reduction of carbon dioxide by hydrogenation to the methanol product (CH_3OH) is at the beginning of study from the point of view of energy applications. The use of methanol for the production of electricity and heat was considered for classical installations and for internal combustion engines (for energy production, including cogeneration), but also in the field of transport and agriculture.
The work as a whole raised specific issue for a circular energy application for the CO_2 component.

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