

Utilization of heat from High Temperature Reactors (HTR) for dry reforming of methane

Krzysztof Jastrzab*

Institute for Chemical Processing of Coal, Zamkowa 1 Str., 41-803 Zabrze, Poland

Abstract. One of the methods for utilization of waste carbon dioxide consists in reaction of methane with carbon dioxide, referred to as dry reforming of methane. It is an intensely endothermic catalytic process that takes place at the temperature above 700°C. Reaction of methane with carbon dioxide leads to formation of synthesis gas (syngas) that is a valuable chemical raw material. The energy that is necessary for the process to take place can be sourced from High Temperature Nuclear Reactors (HTR). The completed studies comprises a series of thermodynamic calculations and made it possible to establish optimum conditions for the process and demand for energy from HTR units. The dry reforming of methane needs also a catalytic agent with appropriate activity, therefore the hydrotalcite catalyser with admixture of cerium and nickel, developed at AGH University of Technology seems to be a promising solution. Thus, the researchers from the Institute for Chemical Processing of Coal (IChPW) in Zabrze have developed a methodology for production of the powdery hydrotalcite catalyser and investigated catalytic properties of the granulate obtained. The completed experiments confirmed that the new catalyser demonstrated high activity and is suitable for the process of methane dry reforming. In addition, optimum parameters of the were process (800°C, CO₂:CH₄ = 3:1) were established as well. Implementation of the technology in question into industrial practice, combined with utilization of HTR heat can be a promising method for management of waste carbon dioxide and may eventually lead to mitigation of the greenhouse effect.

Increasing demand for energy entails growth of interest in nuclear energy. In case of conventional electric power plants energy is produced by nuclear fission and then used for evaporation of superheated steam. Next, the utility is used to generate electricity in steam turbines, similarly to conventional thermal power plants. Nowadays the new generation of nuclear reactors is developed called High Temperature Reactors (HTR) and using neutrons decelerated in a graphic moderator [1]. Such generators produce the intermediate carrier of energy (helium) at the temperature of 600-800°C and are generally engineered for operation in the co-generation arrangement with simultaneous generation of high-temperature process heat and electricity. Thermal energy generated in HTR reactors can be used for a series of

* Corresponding author: kjastrzab@ichpw.pl

high-temperature technological processes, in particular the ones of chemical technologies. The most recent HTR projects are based on the following two key assumptions [2]:

- power is limited to several hundred of thermal megawatts (MWt);
- production of energy carrier with the temperature above 750°C.

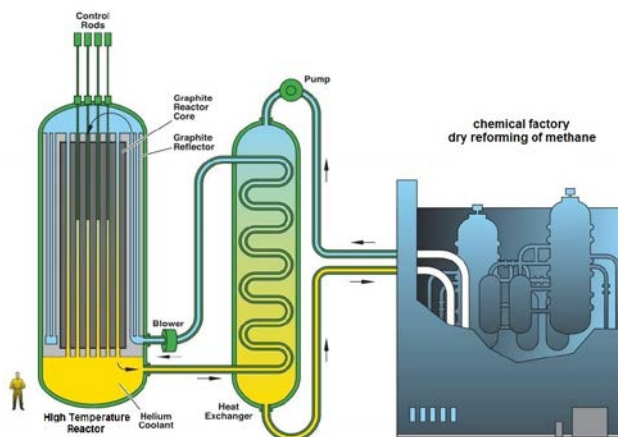


Fig.1. High Temperature Reactor (HTR), source: [Wikipedia](#).

The first High Temperature Reactor (HTR) was operated from 1966 to 1988 at the scientific and research centre Forschungszentrum in Jülich, Germany [3]. Currently one HTR reactor is operated in Japan [4] and subsequent ones are being constructed in China [5]. Also in the USA and in Europe further research studies are in progress to launch HTR units (NGNP consortium and Nuclear Cogeneration Working Group). In Poland the HTRPL [6] project was being executed from 2012 to 2015 within the frameworks of a more extensive program sponsored by the National Centre of Research and Development. The key objectives of the project included examination of opportunities to implement HTR reactors in Poland. The group of industrial partners for the consortium comprises KGHM and TAURON, i.e. large Polish companies, where the first one consumes large amounts of energy whilst the second one is rated among the largest power generators in Poland. The project consortium was completed with such organizations as AGH University of Technology from Cracow, Institute for Chemical Processing of Coal (IChPW) from Zabrze, Central Mining Institute from Katowice, Silesian University of Technology from Gliwice and Institute of New Chemical Syntheses from Puławy.

The contribution of Institute for Chemical Processing of Coal (IChPW) consisted in tasks aimed at establishing of opportunities to utilize heat from HTR units to carry out strongly endothermic chemical syntheses that need application of carbon dioxide. These processes included:

- coal gasification with use of carbon dioxide [7];
- methane reforming with use of carbon dioxide [8];
- utilization of waste CO₂ for the Solvay technology [9].

The foregoing investigations referred to as a reasonable utilization of CO₂ may lead to substantial mitigation of greenhouse effect in future. Emission of CO₂ shall be reduced by both substitution of conventional coal-fired electric power plants with nuclear power plants as well as by conversion of already released carbon dioxide into new chemical products.

The class of strongly endothermal chemical technologies that are popular to enormous scale includes steam reforming of methane:



The synthesis gas originated from the foregoing process (mixture of CO and H₂) is then used for subsequent chemical reactions (production of ammonia, methanol, plastics, etc.).

The interesting modification of the foregoing process consists in reforming of methane by means of carbon dioxide [10] where steam is substituted with carbon dioxide:



It is also a catalytic process with high demand for energy. Similarly to the conventional steam reforming of methane the process balance is substantially shifted to the left side at the temperature below 600°C. It is also the case, i.e. at low temperatures, the hazard of thermal decomposition of methane exists with formation of carbon black, which leads to deactivation of the catalytic agent.

Although the foregoing process has been known for many years it is not implemented yet to the industry. The opportunity to develop the dry reforming technology lies in utilization of heat from HTR units. The additional benefit consists in the possibility to utilize streams of waste CO₂ that is released from conventional power engineering with coal-fired plants or from various chemical processes.

The studies completed within this project included a series of thermodynamic calculations intended to find out equilibrium composition for the post-reaction mixture with consideration of various process parameters. It was demonstrated that the optimum temperature for the dry reforming process of methane is 800°C since the reaction point is sufficiently shifted to the right-hand side. The risk associated with thermal decomposition of methane combined with deactivation of the catalytic agent is then minimized as well. Moreover, to achieve high degree of methane reaction the process should be carried out with the molar ratio between reagents, i.e. CO₂:CH₄ = 3:1.

Thermodynamic calculations made it possible to establish demand of the process in question for energy. The energy is consumed (adsorbed) during two phases (Fig. 2.):

- heating of substrates to the temperature of reaction,
- completion of the reaction at the assumed temperature.

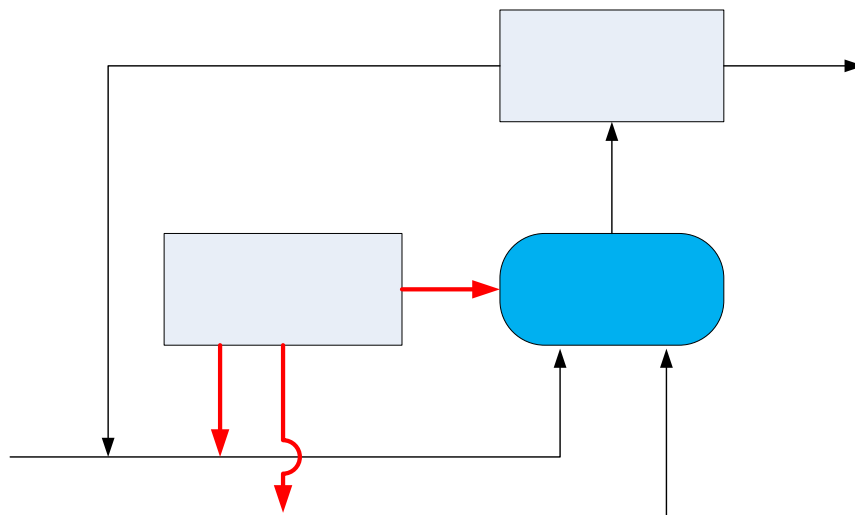


Fig.2. Synthesis gas production via dry reforming of methane using heat of HTR.

The completed calculations confirm that the demand for energy from the process in question is really high, which serve as the justification for use of heat released by HTR units. Results of calculation examples are disclosed in Fig. 3.

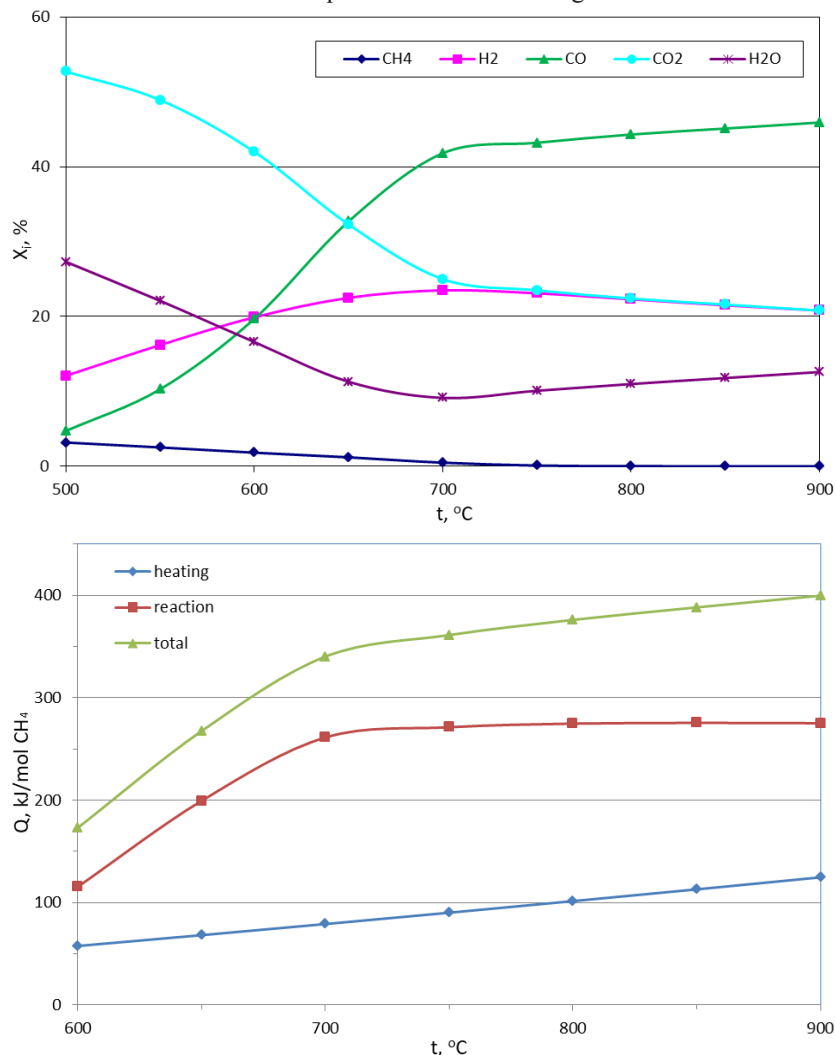


Fig.3. Equilibrium composition of the reaction mixture and energy demand during dry methane reforming as a function of temperature. Exemplary results of thermodynamic calculation at $\text{CO}_2:\text{CH}_4 = 3:1$.

Practical execution of the dry reforming of methane needs a catalytic agent with sufficient activeness. The appropriate catalytic agent enables high reaction rates, which significantly affects dimensions of possible industrial system for dry reforming and its performance. For instance, metallic nickel deposited on purposefully formed aluminium oxide can be used as conventional catalytic agent for the process of steam reforming. Unfortunately, in case of dry reforming such a catalytic agent fails to offer sufficient activeness. It is why seeking for an appropriate catalytic agent are still pending.

Promising properties were revealed for a hydrotalcite catalyser developed by scientists from the AGH University of Technology in Cracow [11]. Hydrotalcite is double-layered mineral with the structure of brucite where a part of magnesium cations is substituted with

aluminium cations according to the isomorphic rule, which makes the general formula $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$. To achieve the desired catalytic properties additional metallic promoters are introduced into the layered structure, for instance nickel or cerium.

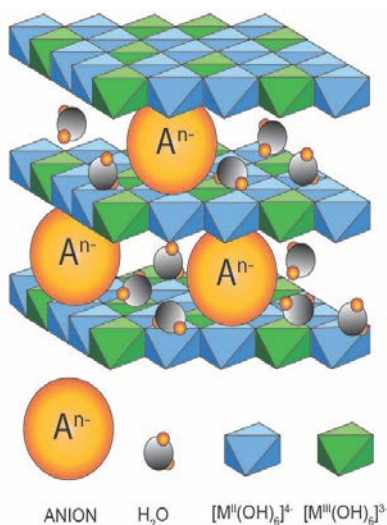


Fig.4. Structure of hydrotalcite.

Upon collaboration with the Faculty of Energy and Fuels at the AGH University of Technology (M. Motak, PhD.) the catalytic agent designated with the symbol of HT10 and with the content of 13% of nickel and 3% of cerium was selected since it proved to be the best catalytic agent for dry reforming of methane. To make its application easier, the technology for granulation of powdery was developed. The final product had five cylinders with the diameters of 5 mm and the length of 10 mm and with sufficient mechanical strength. Eventually, the granulate was used to determine catalytic properties of the catalytic material selected for tests.

The examinations were carried out under laboratory conditions inside a reactor with an immobile bed of catalytic material and a flowing gaseous phase. The reactor diameter was 35 mm whilst weigh of catalytic agent samples placed into the reactor was 50 g. The investigations were carried out for a mixture of methane and carbon dioxide with the total flow of $0.300 \text{ Nm}^3/\text{h}$.

The sample were investigated under the following range of parameters:

- temperatures: 600, 700 and 800°C ;
- molar ratio between CH_4 and CO_2 in the inlet gas: - 1:3, 2:2 and 3:1.

The studies were focused on the analysis of the post-reaction mixture, i.e. the composition of gases at the outlet of the test setup. The particular attention was paid to key reagents: hydrogen and methane. Examples of the analysis results are shown in Fig. 5.

The achieved results served as a confirmation that efficiency of hydrotalcite catalyser and its suitability for the process of dry reforming of methane is really high. The analysis of these results was then used to define optimum conditions for the process execution. The overall objective of the studies was to achieve the maximum degree of methane reaction with high concentration of methane in the post-reaction gas mixture as well as the minimum possible temperature of the chemical process. It was demonstrated that the following parameters are the best suitable for dry reforming of methane:

Temperature of the dry reforming of methane: 800°C
Three times more of CO₂ than CH₄ in the reactive mixture

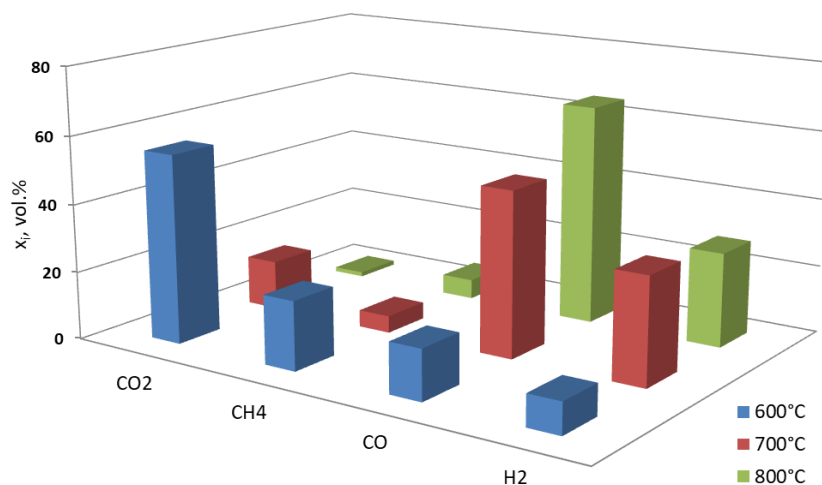


Fig.5. Equilibrium composition of the reaction mixture and energy demand during dry methane reforming as a function of temperature. CO₂:CH₄ = 3:1.

These conditions correspond to the optimum conditions determined on grounds of theoretical calculations. It should be emphasized that the established temperature of the chemical process is the boundary temperature for the circular /intermediate carrier of energy (i.e. helium), the maximum possible one that can be achieved in reactors of HTR type. The results achieved from examinations made it possible to formulate assumptions necessary to design a reference pilot plant for the process of methane reforming with use of carbon dioxide with the capacity of 1000 Nm³ of gas per hour.

It was also demonstrated that the hydrotalcite catalyser activated with nickel and cerium is a material with high catalytic activeness and suitability for the dry process of methane reforming. The process running at the temperature of 800°C and with molar ratio CO₂:CH₄ = 3:1 makes it possible to achieve high degree of reaction with pretty high concentration of hydrogen in the post-reaction mixture (above 50% of H₂ V/V). The optimum temperature necessary for the chemical process and established from these studies enables utilization of heat sourced from nuclear reactors of HTR types is sufficient for both preheating of reagents and for execution of the dry process of methane reforming itself. Implementation of the technology in question into the industrial practice and combining the technology with utilization of heat from HTR units may prove an attractive approach to utilization of waste carbon dioxide and, in consequence, can enable mitigation of the greenhouse effect. Emission of CO₂ shall be reduced by both substitution of conventional coal-fired electric power plants with nuclear power plants as well as by conversion of already released carbon dioxide into new chemical products.

The work was performed under the strategic research project SP/J/1/166183/12 "Development of high-temperature reactors for industrial applications" acronym HTRPL, funded by The National Centre for Research and Development, Poland.

References

1. J. Vujića, R. Bergmanna, R. Škodab, M. Miletićc, *Energy* **45**, 288 (2002)
2. R. Kuhr, *Nuclear Engineering and Design*, **238**, 3013 (2008)
3. <http://www.world-nuclear.org/reactor/default.aspx/AVR Juelich>, received 2017-10-25
4. H. Hayakawa, *Nuclear Engineering and Design* **233**, 391 (2004)
5. Y. Sun, J. Xu, Z. Zhang, *International Journal of Nuclear Hydrogen Production and Applications* **1**, 104 (2006)
6. Strategic research project SP/J/1/166183/12 "*Development of high-temperature reactors for industrial applications*" acronym HTRPL, funded by The National Centre for Research and Development, Poland, 2012-2015
7. K. Jastrzab, O. Piotrowski, *Energy Policy Journal*, **16**, 309 (2013)
8. K. Jastrzab, S. Stelmach, *Cost analysis of using of HTR heat in the process of dry reforming of methane*, Proceedings of the 41th International Conference SSChE, Tatranske Matliare, Slovakia, 2014
9. K. Jastrzab, *Analysis of possibilities of using HTR heat in the Solvay process*, Proceedings of the 43th International Conference SSChE, Tatranske Matliare, Slovakia, 2016
10. T. Chmielniak, M. Ściążko, A. Sobolewski, G. Tomaszewicz, *Energy Policy Journal* **15**, 125 (2012)
11. R. Dębek, A. Gramatyka, M. Motak, P. Da Costa, *Przemysł Chemiczny* **93**, 2026 (2014)