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Modelling of Carbon Monoxide and Carbon Dioxide Methanation under Industrial Condition

Artur Wodołański

Abstract

The development of methanation technology is supported by detailed modeling and process simulation to optimize the design and study of its reaction dynamic properties. The chapter presents a discussion of selected catalysts and its kinetic models in the methanation reaction. The development models of fixed-bed reactors in the methane synthesis were also presented. Chemical and physical modeling of methanation reactions with optimization, exploitation, and the analysis of critical processes in time is an important contribution to the technology modernization.

Keywords: methanation, process design, reactor modeling, catalytic methanation

1. Introduction

Effective transformation of carbon dioxide, which arises when burning fuels in industrial installations on substitution natural gas (SNG), is one of the challenges of the twenty-first century implemented in new research and implementation projects, especially that the pressure of the European Union (EU) to reduce CO₂ emissions increases with every decade. In case of facing problems with carbon capture and storage (CCS) technologies, which are expensive, and at the same time due to the lack of social acceptance for the transport of compressed CO₂ and its underground storage, the European Commission has recently started to suggest the implementation of carbon capture and utilization (CCU) technology or transformation of carbon dioxide into socially acceptable products [1–3].

1970s and 1980s are years, which we were looking for a solution that would turn sulfur into a product like gypsum. Now, we face a similar problem of what to do with carbon dioxide. Industrial methanation processes, which are based on the transformation of carbon dioxide, e.g., from coal-fired power plants and chemical and metallurgical plants or from cement plants to methane as a result of hydrogen-derived water electrolysis fed with surplus cheap energy or from coal gasification [4].

The purpose of the use of surplus energy from wind farms for hydrogen production is to address the problems related to renewable energy sources. A serious drawback of such installations is the lack of human influence on the current volume of production, which depends directly on the forces of nature, i.e., in the case of a wind farm depends on the instantaneous strength of the wind. Hydrogen produced in the process of electrolysis of water, the additional product of which is

oxygen (it can be sold or, for example, used in power coal gasification or for oxygen combustion—in a method that simplifies CO₂ capture). Although, carbon dioxide will come from pilot installations for capturing CO₂ from exhaust gases. CO₂ processing as part of previous research projects in their power plants (mobile installation of amine CO₂ capture in Łaziska Power Plant in a project shared with Tauron PE and variable pressure installation in Łagisza Power Plant) is one of the examples of industrial methanation [5].

A research and development organization CEA deals with CO₂ methanation in modular structural reactors. The first test reactor was started with a capacity of 3–4 m³ CO₂/h at the inlet. One of the companies dealing in the production, purchase of equipment, and their integration with the entire installation will be prepared by West Technology & Trading (deals in the design and construction of industrial installations, among others) [6].

Industrial research and process optimization play an important role in the development and implementation of industrial installations converting CO₂ to methane, which enables effective conversion of CO₂ into methane. CO₂ management options using surplus energy from renewable sources, as well as the possibility of energy storage by converting surplus electricity into a natural gas substitute. All this also increases the stability of the entire energy system, and above all, it is socially acceptable [7].

Among the advantages of the proposed solution, project participants also mention the ease of the use of captured CO₂ without its high compression, transport by pipeline or underground storage, as well as reduction of dependence on natural gas and its imports from outside Europe through the use of gas networks. The risks associated with the project are related to technological issues. This is, for example, the problem of long-term stabilization of the system's efficiency (e.g., catalyst aging) and its durability, as well as the necessity of successful scaling from a demonstration to a commercial installation, for example, on a scale corresponding to the capacity of converting CO₂ from a power unit. However, the key aspect in technology is the type of used catalysts [8]. The chapter presents a model of fixed-bed methanation reactors for one-, two-, and three-dimensional models with a pseudohomogeneous or heterogeneous phase with the application of various kinetic models. The main kinetic models include Kopyscinski, Xu-Froment, van Herwijnen, and van Doesburg. When creating mathematical models, various types of software were used, including MATLAB, OpenFOAM, FEMLAB, Fortran, Modelica, as well as Aspen Plus and ACM. Modeling the methanation reaction allows to effectively predict the rate of methanation reaction depending on the temperature, pressure, or initial concentrations of reagents. Therefore, model research focuses on the modeling of reactions and reactors; however, the reaction mechanism or the degree of catalyst deactivation factors significantly influences the development of the entire process.

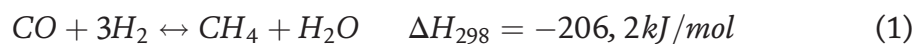
2. Methanation of carbon monoxide catalysis and process kinetics

Carrier metal catalysts play a large role in modern catalysis. They strive to ensure high activity and selectivity in the catalyzed reaction while maintaining stability to ensure their long-term use. The activity of the catalysts is mainly related to the degree of dispersion of the active phase on the support and the state and nature of the interactions between the catalysts and the reactants. Appropriate selection of the catalytic system, preparation conditions, and reaction conditions determines the stability of the catalysts and thus protects against catalyst sintering or poisoning [9].

The CO₂ methanation reaction seems to be interesting for a number of reasons. It allows, among others, the use of waste hydrogen for methane synthesis and removal of traces of CO and CO₂, which are strong poisons of iron catalysts in the ammonia synthesis.

The researchers' interest is usually to determine the effect of various carriers and metals on the efficiency and selectivity of catalysts in the CO₂ methanation reaction, with particular reference to the catalysts obtained on the basis of ruthenium, as well as the selection of optimal conditions for this process [10]. Much work has been devoted to the study of the mechanism of methanation reactions of both oxide and carbon dioxide [11–15]. Carbon oxides are a strong poison of ammonia synthesis catalysts. The methanation process allows to reduce the value of the sum of carbon oxides in the synthesis mixture from 0.2 to 0.5% vol. to below 2 ppmv.

The course of methanation of carbon oxides is described by the following equations of the reaction:



The equilibrium state of both reactions shifts very far to the right side of the equations, and, e.g., at 310°C under atmospheric pressure, the equilibrium concentrations of oxides are about 104 ppm.

For the kinetics and mechanism of CO and/or CO₂ methanation, a cycle of works was devoted. The processes were investigated at atmospheric pressure in a glass cell-free reactor on a NKM-4A catalyst crushed to a grain size of 0.5–1 mm. It was found that CO methanation was much faster than CO₂ methanation according to a different kinetic relationship. The reaction kinetics in the carbon monoxide mixture were complex. CO methane was very poorly controlled by the presence of CO₂, whereas CO₂ methane was strongly inhibited by the presence of CO. From the work, it was concluded that CO methanation-specific activity of nickel depends not only on the nature of the catalyst carrier, but on the methanation of CO₂, and for various catalysts, it varies up to tenfold. Literature information may be an insufficient source of knowledge for industrial process designers as well as for catalyst manufacturers. Therefore, modeling works and reliable information on process kinetics collected on the basis of real reaction rate measurements are important [16].

In most industrial methanation installations, nickel deposited on alumina is used as a catalyst. As a consequence, CO_x methanation reactions on nickel are well understood and described. The industrial process is carried out in the temperature range 250–320°C, under pressure from 1 atm to even several hundreds of atm. The development of more active systems in the methanation reaction may allow for the precise purification of gas from traces of CO_x using a smaller amount of catalyst or reduce the cost of the catalytic charge. This has a major impact on reducing the operating cost of the installation. It is believed that ruthenium is a more active nickel catalyst for the methanation of carbon oxides. In contrast to nickel, which undergoes deactivation at low temperatures due to the formation of carbonyls, ruthenium is stable over a wide temperature range. Commercial ruthenium catalysts for low-temperature methanation of carbon oxides are offered by such producers as Alvigo (RKM-3) or Süd-Chemie (METH 150). Ruthenium systems based on various supports were investigated: aluminum oxide, titanium oxide, or silica. Promising results were obtained using activated carbon as active carriers.

Catalyst (wt.%)	T (°C)	P (bar)	Kinetic approach	Author
Ni/SiO ₂ (60:40%)	260–400	1	Langmuir-Hinshelwood	Burger and Koschany [18]
Ni/SiO ₂ (60:40%)	280–400	30	Langmuir-Hinshelwood	van Meerten [19]
Ni/Cr ₂ O ₃ (62:38%)	160–180	1	Langmuir-Hinshelwood	Kopyscinski [20]
Ni/Al ₂ O ₃ (28:72%)	200–230	1	Power law	Chen [21]
Ni/Al ₂ O ₃ (9% Ni, 1.5% Pt)	260–300	1–5	Power law	Hayes [22]
Ni/SiO ₂ (58:42%)	275–320	17	Langmuir-Hinshelwood	Karolyi [23]
Ni/MgAl ₂ O ₃ (50:50%)	300–400	10	Langmuir-Hinshelwood	Zhang [24]

Table 1.
Kinetic models used in methanation reaction.

Nickel catalysts, supported on a carrier, are commonly used in many important industrial hydrogenation and hydrogenolysis processes, such as methane steam reforming or methanation of synthesis gas, due to the ease of their preparation, high activity, and economic aspects [17]. Nickel catalysts are preferred in the hydrogenation of vegetable oils, edible oils, and the fat industry. Du Bois and other colleagues have designed a nickel complex that is surrounded by amine ligands, which, like in the case of enzymes, enable efficient transfer of protons to nickel atoms. This catalyst is stable and very efficient. Kinetic models used in methanation reaction are presented in **Table 1**.

Catalytic processes, involving a fixed catalyst, so-called contact processes, are the basis of the chemical industry, especially the large-volume industry. It is possible to mention the synthesis of ammonia, oxidation of SO₂ to SO₃, steam reforming of hydrocarbons, conversion of carbon monoxide, catalytic cracking, hydrocracking, or hydrodesulfurization. The catalytic methanation of carbon oxides is used on a large scale for the purification of hydrogen in ammonia synthesis plants. Recently, it has also been proposed to use this reaction for the purification of hydrogen fuels for low-temperature fuel cells.

Kinetics of carbon monoxide methanation on nickel catalysts was examined by Sehested [25], Hayes [22], and van Meerten [19]. Sehested et al. [25] investigated the methanation activity and adsorption of CO and H₂ on a supported Ni catalyst and micrometer-sized Ni threads with a mass of up to 0.4 g at low CO partial pressures (pCO < 25 mbar) in single-pass and recirculation reactors at a total pressure of 1.4 bar (mostly H₂) and temperatures of 225 < T < 400°C. Fujita et al. [26] calculated CO and C coverages in transient response experiments during CO and CO₂ methanation at atmospheric pressure, 200°C, and varying H₂/CO_x ratios in a differential flow reactor containing 1.0 g of Ni catalyst. van Meerten et al. [19] studied kinetics and the mechanisms of methanation of CO on a 5% Ni/SiO₂ catalyst in a differential flow microreactor at 187 < T < 567°C, 133 < pCO < 8.7 × 10⁴. Hayes et al. [22] used a tubular microreactor with a sample mass of up to 1 g at a pressure of 1.3 bar and temperatures of 270 < T < 380°C for dynamic response studies of alumina-supported Ni catalysts prepared by impregnation and coprecipitation.

3. Models of methanation process: fixed-bed reactor development

Chen and Yu [21] built a numerical model of a fixed-bed reactor in which they studied the reaction of CO₂ methanation for the production of synthetic natural gas (SNG).

They developed a numerical model to study the reaction of CO₂ methanation in a tubular reactor with a fixed bed in which the process efficiency was measured. A catalyst consisting of Ni and Ru was used. The reagent temperature in this test was used as the primary parameter at the reactor inlet. Based on the obtained results, it was found that the optimal temperature of the reactant at the inlet appeared at the maximum CO₂ concentration. When the inlet temperature rises above the optimum value, the CO₂ conversion decreases due to the inverse of the Sabatier reaction. The CO₂ conversion can be increased by increasing the working pressure, reactor size, and H₂/CO₂ ratio. CO₂ conversion may also be increased by reducing the feed rate of the reactant. The best H₂ yield can be obtained using a stoichiometric amount of H₂. The introduction of an inert gas into the reactant reduces the CO₂ conversion due to the decrease of CO₂ and H₂ partial pressure. With an isolated reactor and insufficient heat dissipation and high temperature in the reactor, the Sabatier reaction is reversed. The Sabatier reverse reaction caused a decrease in the CO₂ conversion. At low inlet temperature, the heat can be removed, which can lower the reaction temperature, leading to low CO₂ conversion. This confirms the thesis that the Ru-based catalyst has a better performance than the nickel-based catalyst. Bai and Wang [24] studied the effects of the bed aspect ratio, inlet feed temperature, and the pressure in the methanation reactor using coal to synthetic natural gas (SNG) as a model process. A two-dimensional pseudo-homogeneous model was established to simulate the fixed-bed methanation reactor. The numerical model was solved by MATLAB code and validated by an industrial sidestream test. Results show that a bed aspect ratio of 2–3 is helpful to reduce the heat loss below 700°C. A feed temperature of 400°C can accelerate reaction rate and lead to a higher bed temperature of ~800°C. The CO hydrogenation process is dated by operating pressure. The location of the hotspots is equal to 16,000 h⁻¹. When the hydrogen-to-carbon ratio (defined as H₂/(3CO + 4CO₂)) in the feed increases to 2, the CO conversion can be promoted. An increase of the steam-to-gas ratio from 0.19 to 0.4 can effectively control the adiabatic temperature with a hotspot temperature of ~650°C.

3.1 One-dimensional pseudohomogeneous fixed-bed reactor model

Dissinger et al. [27] built a one-dimensional pseudohomogeneous reactor model with adiabatic temperature characteristics, where he used the Fortran programming language to solve numerical equations. van Doesburg [28] built a 1-D pseudohomogenic model using the van Herwijnen kinetic equation with adiabatic temperature characteristics. Er-rbib et al. [29] derived the 1-D model of a pseudohomogenic isothermal reactor using the Kopyscinski kinetic equation [20].

The one-dimensional (1-D) pseudo-homogeneous model of a tubular reactor is described by a system of equations presenting mass and heat balance according to equations:

$$\text{Mass balance : } \frac{\partial(uc_i)}{\partial x} = \rho_{bed} \sum_{j=1}^i v_{i,j} r_j \quad (3)$$

$$\text{Energy balance : } uc_t c_p \frac{\partial T}{\partial x} = \rho_{bed} \sum_{j=1}^i r_j (-\Delta_R H_j) - \frac{4}{d} U(T - T_C) \quad (4)$$

where U is the effective overall heat transfer coefficient, W/m² K; c_p is the specific heat capacity, J/K; T_C is the cooling temperature, K; and d is the tube diameter, m.

This model has gotten the following assumptions: pressure drop along the axial reactor coordinate is neglected, and the partial pressures of the components are calculated assuming ideal gas behavior. The specific heat capacity C_{p_i} is calculated by the Shomate equation.

The 1-D model describing the methanation process, taking into account the mass and heat equations, was formulated by Wasch and Froment [30]. It assumed a series of thermal resistances regarding the heat transfer coefficient and radial heat dissipation. According to the model, radial heat dispersion and effective heat transfer coefficient are characterized by static and dynamics depending on the heat flow areas. When modeling the methanation reaction, the model must meet the following assumptions:

1. Gas mixture is considered ideal.
2. The system is in a steady-state condition.
3. Also, the cross section of the reactor is ideal.
4. Axial mass and heat transfer are assumed to be negligible.

Khorsand and Marvast [31] modelling a methanation catalytic reactor in ammonia unit. The catalytic reactor is similar to that of the steam reforming one. They used orthogonal collocation method to modeling catalytic methanation reaction.

3.2 Two-dimensional pseudohomogeneous fixed-bed reactor model

Schlereth and Hinrichsen [32] used the MATLAB software to build a two-dimensional reactor model using Xu and Froment kinetic equation with a polytropic thermal characteristic.

The two-dimensional (2-D) pseudohomogeneous model of a tubular reactor is described by a system of equations presenting mass and heat balance in accordance with the equations:

$$\text{Mass balance : } \frac{\partial(uc_i)}{\partial x} = \rho_{bed} \sum_{j=1}^i v_{i,j} r_j + D_{eff} \left(\frac{\partial^2 c_i}{\partial r^2} + \frac{1}{r} \frac{\partial c_i}{\partial r} \right) \quad (5)$$

$$\text{Energy balance : } uc_t c_p \frac{\partial T}{\partial x} = \rho_{bed} \sum_{j=1}^i r_j (-\Delta_R H_j) + \Lambda_{eff} \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) \quad (6)$$

They consider the tube's radial coordinate next to the axial one and generally assume axial symmetry, that is, variations of packed beds in angular directions are excluded from consideration. The two-dimensional model gives more detailed information for a quantitative evaluation and the comparison with experimental results. Heat removal from the reactor becomes an important issue to prevent the thermal runaway problem. The model assumes constant values of the property parameter describing pseudo-homogeneous continuity, i.e., the porosity and dispersion coefficients are independent of the radial position of the model. Therefore, it is characterized by heat transfer from the coolant to the inner wall of the pipe (the resistance caused by conduction in the metal wall is neglected). In this model, the introduction of a heat transfer coefficient through the artificial wall for the interior

of the pipe can be avoided because the heat dissipation factor is a function of the radial position and therefore also captures the resistance adjacent to the pipe wall.

The wall heat transfer coefficient and effective heat dispersion coefficient are identical to the contributions of the effective heat transfer coefficient for the 1-D model. The molecular Péclet number is used, and the diffusion coefficient is substituted for the thermal conductivity.

3.3 Heterogeneous reactor model

The 1-D model of the heterogeneous reactor was derived by Bader [33] with adiabatic temperature characteristics using Modelica Fluid software.

Heterogeneous reactors can be simplified by pseudo-homogeneous reactor models, if the effect of external mass transfer and pore diffusion limitations are negligible.

Khorsand et al. [31] used the MATLAB software, where using the kinetic model Xu and Froment to build a 1-D heterogeneous model with adiabatic temperature framework where the catalyst was maintained in isothermal conditions. While in pseudo-homogeneous models, it assumes spontaneously that neither concentration.

There are also no temperature differences between the gas phase and the solid catalyst granules, because only one pseudophase is balanced; the mass and heat balance for both the gas and the solid phases is formulated in heterogeneous models. In this way, the temperature and the concentration differences between phases can be dissolved. Balances for the two-dimensional heterogeneous model of the reactor can be formulated in the following way: they must be formulated separately for the gas phase and separately for the solid phase.

And so for the gas phase:

Mass balance : $\frac{\partial(uc_i)}{\partial x} = D_{eff} \left(\frac{\partial^2 c_i}{\partial r^2} + \frac{1}{r} \frac{\partial c_i}{\partial r} \right) + k$ (7)

Energy balance : $uc_t c_p \frac{\partial T}{\partial x} = \lambda \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) + k_h a (T_s^{pow} - T_C)$ (8)

Reactor dimensions	Phase modeling	Kinetic approach	Software	Authors
1-D	Pseudohomogeneous	van Herwijnen	MATLAB	van Doesburg [28]
1-D	Pseudohomogeneous	Kopyscinski	Aspen Plus	Er-rbib et al. [29]
1-D	Pseudohomogeneous	Kopyscinski	ACM	Güttel [38]
2-D	Pseudohomogeneous	Xu and Froment	MATLAB	Schlereth and Hinrichsen [32]
3-D	Pseudohomogeneous	Measured (first order)	FEMLAB	Cao et al. [35]
0-D	Heterogeneous	Equilibrium	MATLAB	Rönsch et al. [36]
1-D	Heterogeneous	Xu and Froment	MATLAB	Matthischke and Rönsch [36]
1-D	Heterogeneous	Xu and Froment	MATLAB	Parlikkad et al. [37]
1-D	Heterogeneous	Xu and Froment	MATLAB	Schlereth and Hinrichsen [32]

Table 2.
Model characteristics and comparison of fixed-bed methanation reactors.

For the solid phase:

$$\text{Mass balance : } k_m a (c_s^{surf} - c_i) + \rho_{bed} \sum_j^{N_r} v_{i,j} \eta_j r_j^{surf} = 0 \quad (9)$$

$$\text{Energy balance : } k_h a (T_s^{surf} - T_i) + \rho_{bed} \sum_j^{N_r} \eta_j r_j^{surf} (-\Delta H_j) = 0 \quad (10)$$

Schlereth and Hinrichsen stated that the heterogeneous model should be employed, when the catalyst particles are large and have small pore radii or the methanation reactor operates with low Reynolds numbers. Miguel and Mendes [34] developed a kinetic model using industrial nickel-based catalyst. Model characteristics and comparison of fixed-bed methanation reactors was summarized in **Table 2**.

4. Summary and conclusions

In this section, mathematical and numerical models were presented and discussed. It is important to note that analysis of carbon monoxide and carbon dioxide methanation kinetics running in industrial conditions leads to the following conclusions:

- CO methanation rate is about twice as high as methanation CO₂ at the same concentration and temperature.
- The value of exponent at CO concentration, which is dependent on its value and on the range of small concentrations (below concentration around 500 ppm), tends to 1. For higher concentrations, the exponent value is about 0.7.
- Exponent at CO₂ concentration has a constant value of about 0.65 in the entire range of CO₂ concentration tested.
- Values of exponents tend to decrease at the lowest measuring temperature.
- CO methanation rate is not dependent on CO₂ concentration.
- The rate of CO₂ methanation decreases markedly with increasing concentration; thus, the catalyst activity in CO₂ methanation has decisive technological importance.

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