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## MODEL APPROACH OF CARBON DEPOSITION PHENOMENON IN STEAM AND DRY METHANE REFORMING PROCESS

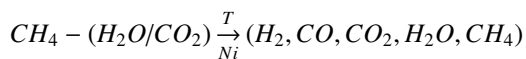
### MODELOWANIE ZJAWISKA WYTRĄCANIA WĘGLA W PROCESIE PAROWEGO I SUCHEGO REFORMINGU METANU

This paper presents thermodynamic conditions for carbon deposition in steam and dry methane reforming process. Ranges of substrate concentrations and temperatures for creating carbon deposition were specified in an analytical form. In the description of the conversion of methane  $\text{CH}_4\text{-H}_2\text{O}$  and  $\text{CH}_4\text{-CO}_2$  parametric equations were used, which allowed to define equilibrium composition of the process. The article formulates the basic assumptions of parametric equations models and their use to describe the course of the homogeneous reactions. The results may provide a model basis for the description of properties of the mixed reforming process  $\text{CH}_4\text{-H}_2\text{O-CO}_2$ .

*Keywords:* steam and dry reforming of methane, carbon deposition, parametric equations, homogeneous reactions described by model of parametric equations

W prezentowanej pracy przedstawiono termodynamiczny warunek wytrącania węgla w procesie parowego i suchego reformingu metanu. Określono zakresy stężenia substratów i temperatury tworzenia depozytów węglowych w postaci analitycznej. Opis konwersji metanu  $\text{CH}_4\text{-H}_2\text{O}$  i  $\text{CH}_4\text{-CO}_2$  zrealizowano z wykorzystaniem formalizmu równań parametrycznych, pozwalającego na określenie składu równowagowego zachodzącego procesu. Przedstawiono podstawowe założenia modelu równań parametrycznych oraz ich wykorzystanie do opisu przebiegu reakcji homogenicznych. Uzyskane wyniki mogą stanowić bazę modelową do opisu własności procesu reformingu mieszanego  $\text{CH}_4\text{-H}_2\text{O-CO}_2$ .

The synthesis gas is used as a raw material for chemical syntheses, a source of pure hydrogen and carbon monoxide [1-4]. It can be obtained in the methane conversion process [1,4,5]. The most common method of syngas production is the steam reforming of methane ( $\text{CH}_4\text{-H}_2\text{O}$ ) with use the catalyst, usually a nickel [1,4]. Yet at present there can be absorbed other methods gaining more and more popularity the so-called dry reforming of methane involving the use of carbon dioxide ( $\text{CH}_4\text{-CO}_2$ ) and the process of mixed reforming with a phase ( $\text{H}_2\text{O/CO}_2$ ) being introduced apart from methane [1,5,6]. Reforming process can be schematically represented as follows [1,2,4-9]:

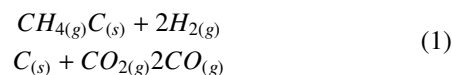


The synthesis gas in addition to hydrogen and carbon monoxide contains unreacted methane, steam and carbon dioxide. An important factor from the point of view of further use of the gas is a parameter that defines the ration between the equilibrium concentration of hydrogen and carbon dioxide (). This ratio depends on temperature and initial ratio of steam to methane for steam reforming and initial ratio of carbon dioxide to methane for dry reforming. Methane conversion  $\text{CH}_4\text{-H}_2\text{O}$  allows to get  $H/C$  about 3 [6,7]. In order to obtain  $H/C \cong 1$

in syngas dry reforming of methane is used and steam-dry methane reforming ( $1 < H/C < 3$ ) is used [2,3,6].

### Thermodynamic approach of carbon deposition phenomenon in methane reforming process

An interesting feature, both from the cognitive and technology point of view, is a possibility to determine the conditions of carbon deposition due to the temperature and initial composition of the process. The cause for the formation of carbon deposits is due to two reactions - the methane thermal cracking and Boudouard reaction [2,4,6,9]:



for which the equilibrium constants denoted by the  $K_M$  and  $K_B$  were calculated from the general relation, where  $\Delta G_T^0$  represents the function of the reaction free enthalpy changes. The gas phase of reforming process includes the reactants ( $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{CO}_2$ ), whose equilibrium concentration ratios are specified by parameters:

$$M = \frac{x_{\text{H}_2}^2}{x_{\text{CH}_4}} \quad B = \frac{x_{\text{CO}}^2}{x_{\text{CO}_2}} \quad (2)$$

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Assuming pure carbon precipitation in the solid phase, we fix that activity of component is equal  $a[C] = 1$ . Given the parameters  $M, B$  and equilibrium constants  $K_M, K_B$  for reaction (1), we get a clear condition that is necessary for the formation of the carbon deposit:

$$[C] = \begin{cases} M \leq K_M \\ B \geq K_B \end{cases} \quad (3)$$

### Determination of the equilibrium compositions of methane reforming process using formalism of parametric equations

From the chemical point of view conversion of methane is quite complex. A description of the methane reforming process prevailing in the specialist literature can be characterized by several reactions shown in the Table 1.

TABLE 1  
Exemplary methane reforming chemical reactions [1,2,6]

Reaction	CH <sub>4</sub> -H <sub>2</sub> O	CH <sub>4</sub> -CO <sub>2</sub>
CH <sub>4(g)</sub> + H <sub>2</sub> O <sub>(g)</sub> ↔ CO <sub>(g)</sub> + 3H <sub>2(g)</sub>	+	-
CO <sub>(g)</sub> + H <sub>2</sub> O <sub>(g)</sub> ↔ CO <sub>2(g)</sub> + H <sub>2(g)</sub>	+	+
CO <sub>2(g)</sub> + 4 H <sub>2(g)</sub> ↔ CH <sub>4(g)</sub> + 2H <sub>2</sub> O <sub>(g)</sub>	+	+
CH <sub>4(g)</sub> + CO <sub>2(g)</sub> ↔ 2CO <sub>(g)</sub> + 2 H <sub>2(g)</sub>	-	+

Detailed interpretation of the determination of the equilibrium composition of the homogeneous reaction, using parametric equations is presented in papers [10,11]. The following are the basic assumptions of parametric equation formalism used in calculations. In a closed system, for isothermal-isobaric conditions, the composition of reaction gas phase varies along the straight line. The transition of reactants from the initial state to the final state (equilibrium) can be marked by the vector parallel to the straight line. For the  $s$ -dimensional space (where  $s$  – number of reagents) parametric equation of a straight line can be written as:

$$x_i = x_i^0 + \tau \cos \alpha_i \quad i = 1, \dots, s \quad (4)$$

where:  $x_i$  – equilibrium and initial molar fraction of a component „ $i$ ”,  $\alpha_i$  – direction angles,  $\tau$  – parameter, .

Direction cosine of a line can be expressed in the following form:

$$\cos \alpha_i = \frac{k_i - x_i^0 \sum_{i=1}^s k_i}{\sqrt{\sum_{i=1}^s \left( k_i - x_i^0 \sum_{i=1}^s k_i \right)^2}} \quad i = 1, \dots, s \quad (5)$$

where:  $k_i$  – stoichiometric coefficient of reactant „ $i$ ”.

Directional cosines of the vector do not depend on time. They depend only on initial composition and stoichiometric coefficients of the reaction. In the case of a non-equimolar reaction ( $\sum_{i=1}^s k_i \neq 0$ ), the parametric equation (4) can be presented as:

$$x_i = x_i^0 + \tau (\bar{x}_i - x_i^0) \quad i = 1, \dots, s \quad (6)$$

where:  $\bar{x}_i$  – characteristic point of the reaction defined as:

$$\bar{x}_i = \frac{k_i}{\sum_{i=1}^s k_i} \quad i = 1, \dots, s \quad (7)$$

The characteristic point for the gas not involved in the reaction is zero, while the concentration of this component changes during the reaction. For equimolar reactions ( $\sum_{i=1}^s k_i = 0$ ) equation (4) reduces to the form:

$$x_i = x_i^0 + \tau \frac{k_i}{\sqrt{\sum_{i=1}^s (k_i)^2}} \quad i = 1, \dots, s \quad (8)$$

This relation is called a characteristic formula of chemical reaction. Directional cosine does not depend on initial composition, it depends only on the stoichiometric coefficients. In this case, the inert gas concentration does not change during the reaction.

### Calculation procedure

The equilibrium compositions of both steam and dry reforming of methane were defined using the calculation: change of standard Gibbs free energy  $\Delta G_T^0$ , the value of the equilibrium constant  $K$  and parametric equations set. The results were obtained for the standard pressure  $P = 10^5$  [Pa], temperature range  $T$  (800K, 1200K) and for the initial composition represented by the  $SC$  (for steam reforming) or  $CC$  (for dry reforming). Numerical calculations were performed using numerical computing environment MATLAB based on the thermodynamic data [12]. For a given type of methane reforming, the first step was to create a parametric equation for the model reactions, taking into account all the components involved in the process (H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O). For defined by the  $SC$  or  $CC$  initial composition  $x_i^0$  equilibrium composition was found for the first model reaction. The parameter  $\tau$  is calculated by substituting appropriate parametric equations into equilibrium constant  $K$ . Amid the searched parameters  $\tau$  only this one had a physical sense for which conditions  $0 < x_i < 1$  and  $\sum_{i=1}^s x_i$  were satisfied. Afterwards, the equilibrium composition of the first reaction became an initial composition for the second reaction and the equilibrium composition of this reaction became an initial composition for next reaction. For example, Figure 1 shows a flowchart for calculation of dry reforming reaction. Since it was assumed that all reactions in the process occur parallel to each other, the final composition must meet all of the equilibrium constants for the model reactions. For this purpose, the calculation was carried out in the loop until the condition was satisfied and the final composition of the process was obtained.

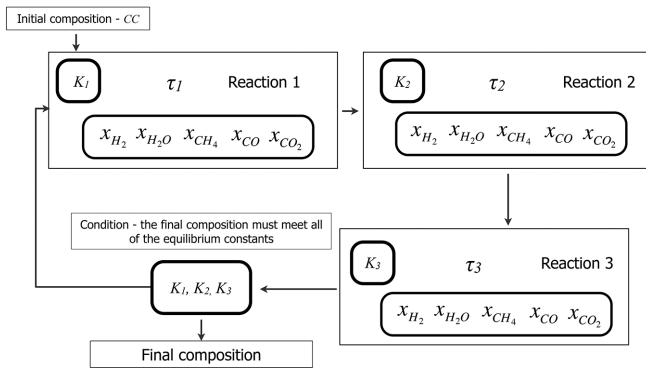


Fig. 1. Flowchart for dry reforming of methane numerical calculation

With complete information on the equilibrium compositions of methane reforming process, calculated by the procedure of parametric equations, according to the condition (3) specified the range of creating field of the carbon deposition in the process. For this purpose, an independent variable, determining the composition of the gaseous mixture introduced into the conversion of methane with steam or carbon dioxide, was defined as follows:

$$\begin{aligned} x_{H_2O, CO_2}^0 &= y \\ x_{CH_4}^0 &= 1 - y \end{aligned} \quad (9)$$

Defining of analytical relations between the initial composition  $y_{[C]}$  and temperature input for which it comes to carbon composition was based upon the second degree polynomial function:

$$-T \ln(y_{[C]}) = \sum_{j=0}^n A_j T^j + A_{n+1} T \ln(T) \text{ for } n = 2 \quad (10)$$

Using functions  $-T \ln(y_{[C]})$  and form of the polynomial function were to help to reveal all possible irregularities in the course of the relation  $y_{[C]} = f(T)$  and ensure the maximum accuracy of the description. The values of polynomial coefficients  $A_j$ , were obtained by minimizing the expression:

$$\varphi = \sum \left[ -T \ln(y_{[C]}) - \sum_{j=0}^n A_j T^j + A_{n+1} T \ln(T) \right]^2 \text{ for } n = 2 \quad (11)$$

and summarized in tabular form (Table 2).

TABLE 2

Polynomial coefficients for relation between temperature and substrates concentration in steam and dry reforming of methane in carbon deposition area

Type of reforming	$A_0$	$A_1$	$A_2$	$A_3$
CH <sub>4</sub> – H <sub>2</sub> O	35034.29	-495.597	-0.036113	71.992378
CH <sub>4</sub> – CO <sub>2</sub>	76987.19	-1105.825	-0.081149	160.74861

Consequently, the range of substrate concentration for steam and dry reforming of methane in the range of technological temperature  $T \in (800K, 1200K)$ , at which the carbon deposition formed in a process is characterized by the equation:

$$y_{[C]}(T) = \exp\left[-\frac{1}{T} \left( \sum_{j=0}^n A_j T^j + A_{n+1} T \ln(T) \right)\right] \text{ for } n = 2 \quad (12)$$

The Figure 2 presents a graphical illustration of polynomial and model approach using the formalism of parametric equations applied to the description of the carbon deposition area. The maximum difference in the polynomial description and model results  $y_{[C]}$  in the analyzed temperature range  $T \in (800K, 1200K)$ , does not exceed  $\Delta T_{\max.} = 3 K$ .

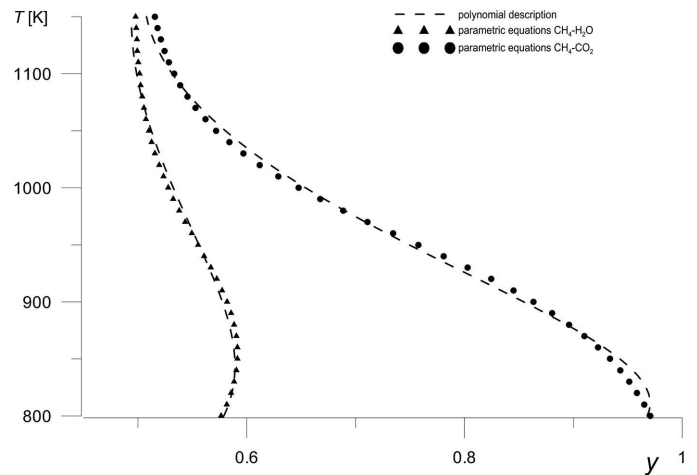


Fig. 2. Boundaries of carbon deposition area of steam and dry methane reforming

## Summary

Model approach presented in this article, describing steam and carbon dioxide conversion of methane using a formalism of parametric equation that can provide the basis for empirical research of methane reforming process. The unambiguous thermodynamic condition of carbon deposition was obtained. Concentration and temperature ranges associated with this phenomenon were specified in an analytical form, which allowed reduce time-consuming and expensive experimental procedure. In drawing upon the existing base model, one can continue further research in an interesting and utilitarian direction, related to the recognition of a model of steam-dry reforming process CH<sub>4</sub>-H<sub>2</sub>O-CO<sub>2</sub>.

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