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MODEL APPROACH OF CARBON DEPOSITION PHENOMENON IN MIXED H_2O/CO_2 METHANE REFORMING PROCESS

MODELOWANIE ZJAWISKA WYTRĄCANIA WĘGLA W PROCESIE REFORMINGU METANU FAZĄ GAZOWĄ H_2O/CO_2

This paper presents thermodynamic conditions for carbon deposition in methane reforming process by gas phase H_2O/CO_2. Ranges of substrate concentrations and temperatures for creating carbon deposition were specified in an analytical form. In the description of the conversion of methane CH_4-(H_2O/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 CH_4 – (H_2O/CO_2).

Keywords: 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 reformingu metanu fazą gazową H_2O/CO_2. Określono zakresy stężenia substratów i temperatury tworzenia depozytów węglowych w postaci analitycznej. Opis konwersji metanu CH_4-(H_2O/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 tzw. procesu reformingu mieszanego CH_4 – (H_2O/CO_2).

1. Introduction

The most common method of syngas production which is a raw material for chemical syntheses, a source of pure H_2 and CO is the steam reforming of methane (CH_4 - H_2O) with use the catalyst, usually a nickel one [1-5]. Also so-called dry reforming of methane with carbon dioxide (CH_4-CO_2) is used. 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 monoxide ($H/C = x_{H_2}/x_{CO}$). This ratio depends on temperature and initial ratio of steam to methane $SC = x^0_{H_2O}/x^0_{CH_4}$ for steam reforming and initial ratio of carbon dioxide to methane $CC = x^0_{CO_2}/x^0_{CH_4}$ for dry reforming. Methane conversion CH_4-H_2O 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 [2,3,6]. Yet at present so-called mixed reforming with a phase (H_2O/CO_2) introduced apart from methane gains more and more popularity in the technology of syngas production [1,5,6]. This option of the conversion of methane allows to obtain the parameter H/C in the range 1÷3 [2,3,6]. Reforming process can be schematically represented as follows [1,2,4-8]:

$$CH_4 - (H_2O/CO_2) \xrightarrow[Ni]{T} (H_2, CO, H_2O, CO_2, CH_4)$$

2. 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]:

$$\begin{gathered} CH_{4(g)} \leftrightarrow C_{(s)} + 2H_{2(g)} \\ C_{(s)} + CO_{2(g)} \leftrightarrow 2CO_{(g)} \end{gathered} \tag{1}$$

for which the equilibrium constants denoted by the K_M and K_B were calculated from the general relation $\Delta G^0_T = -RT\ln(K)$, where ΔG^0_T represents the function of the Gibbs free energy changes. The gas phase of reforming process includes the

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TABLE 1

Exemplary reforming reactions of methane CH_4-H_2O-CO_2

Reaction	CH_4- H_2O	CH_4- CO_2	CH_4 - (H_2O/CO_2)
$CH_{4(g)} + H_2O_{(g)} \leftrightarrow CO_{(g)} + 3H_{2(g)}$	+	-	-
$CO_{(g)} + H_2O_{(g)} \leftrightarrow CO_{2(g)} + H_{2(g)}$	+	+	+
$CO_{2(g)} + 4\ H_{2(g)} \leftrightarrow CH_{4(g)} + 2H_2O_{(g)}$	+	+	+
$CH_{4(g)} + CO_{2(g)} \leftrightarrow 2CO_{(g)} + 2\ H_{2(g)}$	-	+	-
$2CH_{4(g)} + H_2O_{(g)} + CO_{2(g)} \leftrightarrow 3CO_{(g)} + 5H_{2(g)}$	-	-	+

reactants (H_2, H_2O, CH_4, CO, CO_2), whose equilibrium concentration ratios are specified by parameters:

$$M = \frac{x_{H_2}^2}{x_{CH_4}} \quad B = \frac{x_{CO}^2}{x_{CO_2}} \tag{2}$$

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:

$$[C] = \begin{cases} M \leqslant K_M \\ B \geqslant K_B \end{cases} \tag{3}$$

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.

Detailed interpretation of the determination of the equilibrium composition of the homogeneous reaction, using parametric equations is presented in papers[9,10]. The following are the basic assumptions of parametric equation formalism used in calculations. Any chemical reaction can be described by the equation:

$$\sum\nolimits_{i=1}^{s} k_i B_i = 0 \qquad i = 1, \ldots, s \tag{4}$$

where: B_i – reaction reactants, k_i – stoichiometric coefficients of reactants.

For products, positive values for the stoichiometric coefficients are assumed, for substrates negative, and for reagents not taking part in a chemical reactions the stoichometric coefficients are zero. 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:

$$x_i = x_i^0 + \tau \cos\alpha_i \qquad i = 1, \ldots, s \tag{5}$$

where: x_i, x_i^0 – equilibrium and initial molar fraction of a component „i”, α_i – direction angles, τ – parameter, $\tau \in R$.

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

$$\cos\alpha_i = \frac{k_i - x_i^0 \sum\limits_{i=1}^{s} k_i}{\sqrt{\sum\limits_{i=1}^{s} \left(k_i - x_i^0 \sum\limits_{i=1}^{s} k_i\right)^2}} \qquad i = 1, \ldots, s \tag{6}$$

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:

$$x_i = x_i^0 + \tau\left(\bar{x}_i - x_i^0\right) \quad i = 1, \ldots, s \tag{7}$$

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

$$\bar{x}_i = \frac{k_i}{\sum\limits_{i=1}^{s} k_i} \quad i = 1, \ldots, s \tag{8}$$

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:

$$x_i = x_i^0 + \tau \frac{k_i}{\sqrt{\sum\limits_{i=1}^{s} (k_i)^2}} \quad i = 1, \ldots, s \tag{9}$$

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.

4. Calculation procedure

The equilibrium compositions of mixed reforming of methane by gas phase CH_4 – (H_2O/CO_2) were defined using the calculation: change of standard Gibbs free energy , the value of the equilibrium constant K and parametric equations set. The results were obtained for the standard pressure $P = 10^5$ [Pa] and temperature range T (800 K, 1200 K). Independent variables, determining the initial composition of the gas mixture introduced into the methane reforming process, defined as follows (Fig. 1):

$$y = 1 - x^0_{CH_4} \quad t = \frac{x^0_{CO_2}}{x^0_{H_2O} + x^0_{CO_2}} \tag{10}$$

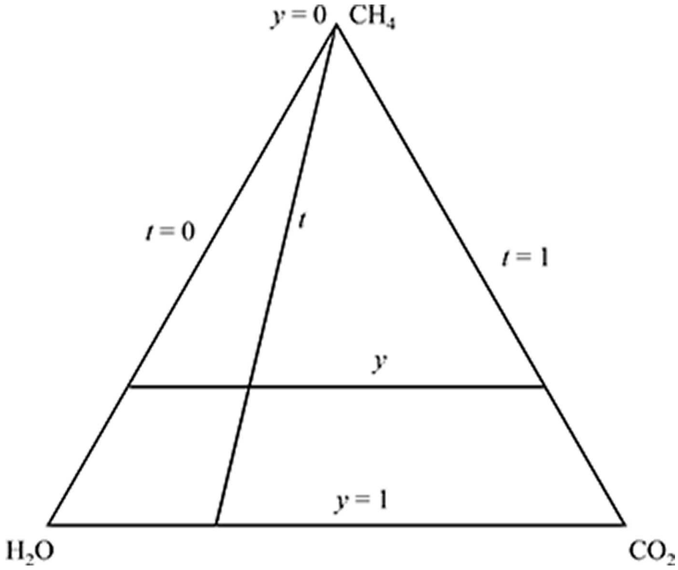

Fig. 1. Initial composition of the gas mixture $CH_4 - H_2O - CO_2$ as a function of t and y

The concentrations of the ingredients put into the conversion process can be expressed by t and y in form:

$$x^0_{CH_4} = 1 - y$$

$$x^0_{H_2O} = (1 - t)y$$

$$x^0_{CO_2} = ty$$

t values are constant along the lines of a fixed ratio $x^0_{CO_2}/x^0_{H_2O}$. These values vary from $t = 0$ (steam reforming CH_4-H_2O) for $t = 1$ representing the conversion of methane by carbon dioxide (CH_4-CO_2). The parameter $y = \text{const.}$ specify lines parallel to the base of the triangle ($y = 1$) defining a ratio of the concentrations of carbon dioxide and steam introduced into the process. If $y = 0$ we have a pure component which is methane. Numerical calculations were performed using numerical computing environment MATLAB based on the thermodynamic data [11]. The first step of analysis was to create a parametric equation for the model reactions, taking into account all the components involved in the process (H_2, CO, CO_2, CH_4, H_2O). For defined by the t and y initial composition x^0_i equilibrium composition was found for the first model reaction. The parameter τ is calculated by substituting appropriate parametric equations into equilibrium constant K. Amid the searched parameters τ only this one had a physical sense for which conditions $0 \leqslant x_i \leqslant 1$ and $\sum_{i=1}^{2} x_i = 1$ 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 2 shows a flowchart for calculation of dry reforming process ($t = 1$). 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.

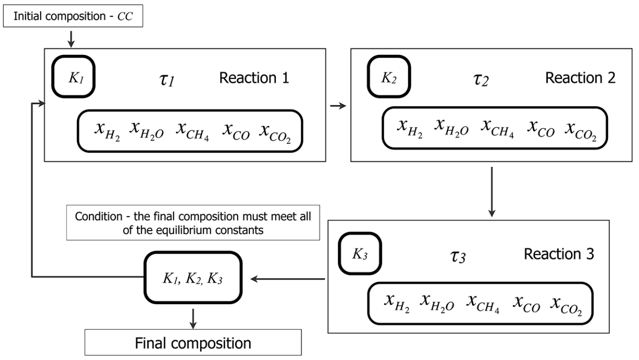

Fig. 2. Flowchart for dry reforming of methane numerical calculation

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. Database of $y_{[C]} = f(T,t)$ in numerical form was obtained. Defining of analytical relations between the initial composition $y_{[C]}$ and temperature, parameter t for which it comes to carbon composition was based upon the polynomial function. For this purpose, for the established temperature $T = \text{const.}$ relation $-T\ln(y_{[C]})$ as a function of t is described by the third degree polynomial, taking into account boundary conditions $t = 0$ and $t = 1$:

$$-T\ln(y_{[C]}) = \sum\nolimits_{j=0}^{3} A_j t^j \quad j = 0, \ldots, 3 \tag{11}$$

where for:

$t = 0 \quad A_0 = A_j$ (steam reforming CH_4-H_2O)

$t = 1 \quad A_0 + A_1 + A_2 + A_3 = A_j$ (dry reforming CH_4-CO_2)

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

$$\varphi = \sum \left[-T\ln(y_{[C]}) - \sum\nolimits_{j=0}^{3} A_j t^j\right]^2 \quad j = 0, \ldots, 3 \tag{12}$$

and summarized in tabular form (Table 2). Whereas, a graphical illustration of polynomial approach used to describe $-T\ln(y_{[C]}) = f(t)$, for $T = \text{const.}$ is presented in Figure 3.

In the next stage, relation between coefficients A_j obtained from equation (11) and temperature in the range $T \in (800, 1200)$ K was defined. This relationship is shown in the form of a power series:

$$A_j = \sum\nolimits_{i=0}^{2} a_{ji} T^i + a_{j,3} T\ln(T) \quad j = 1, \ldots, 3 \tag{13}$$

TABLE 2

Polynomial[11] coefficients A_j for T = const.

T [K]	A_j			
	$j = 0$	$j = 1$	$j = 2$	$j = 3$
800	440.62	-915.37	654.21	-155.17
850	446.33	-683.95	322.38	-25.98
900	487.16	-499.64	116.39	28.36
950	558.48	-343.53	22.15	26.74
1000	638.65	-214.52	-0.12	10.60
1050	707.01	-125.71	-0.24	5.45
1100	759.17	-69.78	-0.59	2.44
1150	801.72	-46.91	13.09	-5.86
1200	839.00	-31.28	10.48	-3.26

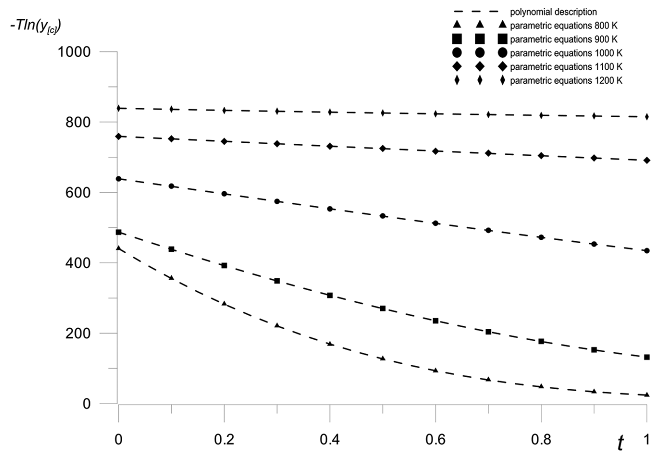

Fig. 3. Function $-T\ln(y_{[C]}) = f(t)$, for T = const. according to polynomial and parametric equation description

Coefficients a_{ji}, calculated using the last square method are provided in Table 3.

TABLE 3

Coefficients of equation $y_{[C]} = f(t,T)$

j	a_{ji}			
	$i = 0$	$i = 1$	$i = 2$	$i = 3$
0	35034.29	-495.5973	-0.03611	71.9924
1	-15829.52	113.5924	0.00079	-14.2991
2	110516.66	-1431.8525	-0.09469	204.9898
3	-52671.64	707.5229	0.04886	-101.8695

In this way, the relationship $-T\ln(y_{[C]}) = f(T, t)$ was defined and summarized as expressed in the equation:

$$-T\ln(y_{[C]}) = \sum_{j=0}^{3}\left(\sum_{i=0}^{2} a_{ji}T^{i} + a_{j,3}T\ln(T)\right)t^{j} \qquad (14)$$

Consequently, the range of substrate concentration for methane reforming by gas phase H_2O/CO_2 in the range of technological temperature $T \in (800\ K, 1200\ K)$, at which the carbon deposition formed in a process is, characterized by the equation:

$$y_{[C]}(T,t) = \exp\left\{-\frac{1}{T}\left[\sum_{j=0}^{3}\left(\sum_{i=0}^{2} a_{ji}T^{i} + a_{j,3}T\ln(T)\right)t^{j}\right]\right\} \qquad (15)$$

The Figure 4 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 results $y_{[C]}$ in the model approach with use of parameter equations in the analyzed temperature range $T \in (800\ K, 1200\ K)$, does not exceed $\Delta T_{max.} = 3$ K.

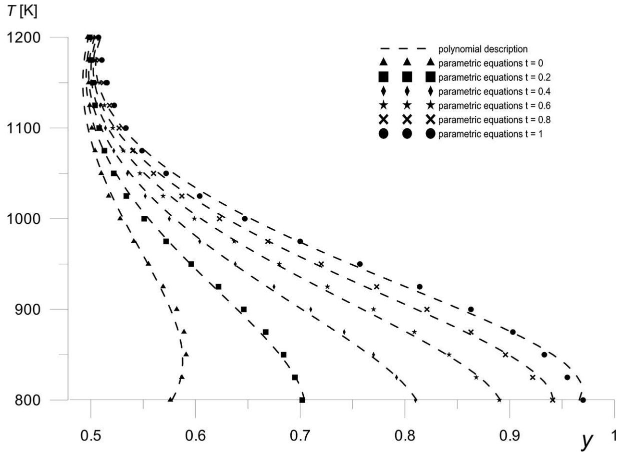

Fig. 4. Boundaries of carbon deposition area of methane reforming process by gas phase $CH_4 - H_2O - CO_2$

5. Conclusions

Model approach presented in this article, describing conversion of methane using a formalism of parametric equation can provide the basis for empirical research of methane reforming process by gas phase H_2O/CO_2. 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 $CH_4 - H_2O - CO_2$.

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