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CRITICAL ANALYSIS OF UNDERGROUND COAL GASIFICATION MODELS. PART I: EQUILIBRIUM MODELS – LITERARY STUDIES

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ABSTRACT

Purpose	Underground coal gasification is a very difficult process due to changes in the parameters over time and within the space of the reactor and a variety of phenomena that occurs there. Consequently, it is necessary to create appropriate mathematical models, which simplify the optimization and forecast of future results (especially final gas properties). The purpose of this work was the detailed critical analysis of the simplest coal gasification simulations methods, based on thermodynamic calculations of the process. These models, called equilibrium models, can be divided into two groups: stoichiometric and non-stoichiometric. The other aim of this paper was to characterize various engineering methods used in the calculation of equilibrium gasification processes.
Methods	Literary studies, concerned with general aspects of underground coal gasification modeling and the modeling of coal gasification in the manner of equilibrium calculations, were used as a research method applied in presented work.
Results	The critical analysis of equilibrium models of coal gasification and the characterization (including mathematical formulation of process, range of required parameters, rate of convergence of calculations and methodology of searching solutions) of stoichiometric and non-stoichiometric methods were results of numerous considerations presented in this article.
Practical implications	The work presented describes practical issues connected with equilibrium models – their advantages, limitations and possible problems (for example with the determination of required constants) and potential applications (preliminary analysis, point of reference to more complex simulations etc.).
Originality/value	This paper presents state of the art in field of equilibrium coal gasification modeling. This article is also attempt to elaborate on the most important problems connected with thermodynamic models of coal gasification.

Keywords

coal gasification, equilibrium, stoichiometric model, non-stoichiometric model

1. INTRODUCTION

Underground coal gasification (UCG), defined as production of gaseous fuels carried directly in coal seam, may be an attractive alternative to surface processes. Firstly, UCG can be used to utilize coal seams which could not be exploit by conventional technologies (too deep or steeply dipping, low rank coals). In comparison to surface gasification, UCG offers lower capital and operating costs, a reduction in underground human labour and environmental benefits (Bhutto, Bazmi, & Zahedi, 2013).

On the other hand underground coal gasification is a complex and technically challenging process. Most of its parameters are changing both during the time of gasification and within the space of the reactor (Kapusta & Stańczyk, 2009). Moreover UCG is determined not only by a complex set of

chemical reactions but also by lots of physicochemical processes, like heat and mass transfer, turbulent mixing, cavity growth and flow through the porous medium. What is more, the same coal is raw material whose properties cannot be strictly characterized, because of their dependence on rank and place of exploitation of the analyzed fuel (Golec & Ilmurzyńska, 2008; Nitao et al., 2011).

The management and running of UCG process will be possible provided that physical and chemical phenomena occurring in gasification and factors effecting them are recognized. Unfortunately, experiments carried out directly in underground reactors are expensive and in some cases impossible to perform. Therefore computer simulations of gasification processes become increasingly significant in science and the industry in general. An appropriate mathematical model will enable not only the theoretical characterization of pro-

cess and its results (which will provide a better understanding of the mechanisms of the process) but also a choice of optimal gasification parameters in order to obtain syngas with suitable properties – chemical composition and heat value (Bialecka, 2008; Wachowicz, Janoszek, & Iwaszenko, 2010).

2. MODELING OF UNDERGROUND COAL GASIFICATION – BASIC REMARKS

Underground coal gasification is a process which requires taking many essential decisions, such as: site selection, the geometry of the reactor, the composition and injection rate of the gasifying agent and environmental monitoring. An ideal UCG model should predict each important aspects of the process, e.g.:

- syngas composition and heat value,
- cavity growth,
- water influx to reactor,
- roof collapse and subsidence,
- transport of contaminants out of the reactor (Nitao et al., 2011).

However, due to the complexity of the phenomena occurring during gasification, every model is only an approximation of reality, describing chosen elements of the process. This article presents analysis of UCG models which concentrate on predicting syngas composition.

It is widely known that processes of underground coal gasification should be proceed in a way which provides to obtain syngas with the highest amount of combustible compounds – CO, H₂, CH₄ and the lowest amount of non-combustible components. It is a very complicated issue, because the final composition of the produced gas depends on many factors, like the properties of the gasifying agent and the analyzed fuel, features of the coal seam and the parameters of the same process (temperature and pressure). Unfortunately, determining their level of importance is extremely difficult. What is more, the aforementioned mentioned factors may positively affect one fraction of the process parameters and negatively on the other part (Żogała, Kabiesz, & Iwaszenko, 2013).

There are a lot of UCG models which vary in level of detail of included phenomena, rate of convergence, mathematical procedures and the required input parameters. These models can be divided into equilibrium models, kinetic models and CFD (*Computational Fluid Dynamics*) models (Golec & Ilmurzyńska, 2008).

This paper presents only the equilibrium approach used in simulations of gasification processes. Kinetic and computational fluid dynamics models were analyzed in a separate part of the article.

3. EQUILIBRIUM MODEL

Equilibrium models are based on the thermodynamic analysis of gasification processes. This kind of model assumes that the system reaches a state of equilibrium, which means that the rate of chemical reaction is infinitely fast or the time of reaction is appropriately long (Golec & Ilmurzyńska, 2008).

Equilibrium models of gasification use two general approaches, which vary in the method of formulation of set of equations (describing the state of equilibrium) and scope of input data. The first of them, the stoichiometric model, is based on mass-action law and the equilibrium constants of

chemical reactions. The second model, non-stoichiometric, minimizes the Gibbs free energy of the analyzed system.

The non-stoichiometric method is more general – information about the number and kind of independent reactions and values of equilibrium constants is not necessary. Therefore this model can be used for every case. However it is computationally more complicated because the determination of the minimum of Gibbs free energy is not easy, it requires a long time to calculate, and consequently simulation converges with a lower rate.

The stoichiometric method is computationally simpler and a faster convergent than the non-stoichiometric method. On the other hand it is less general – limited to one set of reactions. Therefore when additional species is included in the process, the whole procedure must be modified (Kozaczka, 1994).

3.1. Stoichiometric model

The stoichiometric model of gasification involves defining the following inputs:

- parameters of process (pressure and temperature),
- initial composition of reacting mixture,
- number and kind of independent reactions.

Providing that seven components: C, CO, CO₂, H₂O, H₂, CH₄, O₂ take part in gasification, the system is described by chemical matrix **A**:

element \ compound	C	O	H
C	1	0	0
CO	1	1	0
CO ₂	1	2	0
H ₂	0	0	2
H ₂ O	0	1	2
CH ₄	1	0	4
O ₂	0	2	0

$A =$ (1)

The rank of this matrix is equal to $R(\mathbf{A}) = 3$. For the reason that the number of independent chemical reactions is difference between the amount of mixture components and rank of the chemical matrix, the system is determined by four reactions (Tabiś, 2002).

Common calculating methods are generally bases on the following reactions:



The selected chemical model requires the determination of the values of equilibrium constants of the chosen reactions for the defined temperature (T) of the process. It may be done by calculating the Gibbs free energy for the analyzed reaction ($\Delta_R g^\circ$). In this way the procedure of computing the equilibrium constant is described by the following algorithm:

1. Collection of thermodynamic data for a particular reactant **i**: specific heat ($c_{p,i}$)¹, enthalpy ($\Delta_R H_{i,298}^\circ$) and entropy ($\Delta_R S_{i,298}^\circ$) in standard temperature ($T = 298$ K).

¹ Specific heat of reactant **i** is determined in thermodynamic tables by coefficients of polynomial $c_{p,i} = A_i + B_i T + C_i T^{-2} + D_i T^2$.

2. Calculation of enthalpy ($\Delta_R h_{298}^\circ$) and entropy ($\Delta_R s_{298}^\circ$) of reaction in standard temperature from the following equations²:

$$\Delta_R h_{298}^\circ = \sum_i v_i \Delta H_{298}^\circ \quad \text{and} \quad \Delta_R s_{298}^\circ = \sum_i v_i \Delta S_{298}^\circ \quad (6)$$

3. The determination of coefficients of the specific heat of the reaction ($\Delta_R c_p$):

$$\Delta_R c_p = \alpha + \beta T + \gamma T^{-2} + \delta T^2 \quad (7)$$

where $\alpha = \sum_i v_i A_i$, $\beta = \sum_i v_i B_i$, $\gamma = \sum_i v_i C_i$ and $\delta = \sum_i v_i D_i$.

4. Computation of enthalpy ($\Delta_R h^\circ$) and entropy ($\Delta_R s^\circ$) of reaction at a given temperature as:

$$\Delta_R h^\circ = \Delta_R h_{298}^\circ + \int_{298}^T \Delta_R c_p dT \quad \text{and} \quad \Delta_R s^\circ = \Delta_R s_{298}^\circ + \int_{298}^T \frac{\Delta_R c_p}{T} dT \quad (8)$$

5. Calculation of Gibbs free energy of the reaction as:

$$\Delta_R g^\circ = \Delta_R h^\circ - T \Delta_R s^\circ \quad (9)$$

6. Computation of the equilibrium constant from the following equation (where R is universal gaseous constant):

$$K_p = \exp\left(-\frac{\Delta_R g^\circ}{RT}\right) \quad (10)$$

Equilibrium constant may also be expressed with mole fractions of the components (x_i):

$$K_x = \prod_i x_i^{v_i} \quad (11)$$

Providing that the system is determined by r number of reactions, mole fractions of the components are calculated as:

$$x_i = \frac{n_{0i} + \sum_r v_{i,r} \xi_r}{n_0 + \sum_r v_r \xi_r} \quad (12)$$

where:

- n_{0i} – initial amount of moles of reactant i , kmol;
- n_i – current amount of moles of reactant i , kmol;
- $v_{i,r}$ – stoichiometric coefficient of reactant i in reaction r [-];
- ξ_r – extent of reaction r , kmol³;

$$\text{and } n_0 = \sum_i n_{0i}, \quad v_r = \sum_i v_{i,r}$$

Equilibrium constant, depending on pressure, can be calculated as:

$$K_p = K_x p^{\sum v_i} \quad (13)$$

In following step of calculations equation (10) is compared to equation (13). It is necessary to create as many equations as independent reactions have been determined. The set of equations formed in this way is worked out for ξ_r (Kozaczka, 1994; Tabiś, 2002).

Practical calculation methods are based on a set of equations including equilibrium constant expressions and balance of elements occurring in the system (Kozaczka, 1994).

For example, the Bourdouard reaction describes the simplest case of gasification, where only CO₂ and CO appear in the reacting system. Equilibrium composition of syngas can be calculated from the following set of equations:

$$\begin{cases} x_{\text{CO}} + x_{\text{CO}_2} = 1 \\ K_p = \frac{x_{\text{CO}}^2}{x_{\text{CO}_2}} p \end{cases} \quad (14)$$

When syngas contains more species, it necessary to take into account more equations and unknowns (Petela, 1969). The characterization of several engineering methods of calculating equilibrium gasification processes is given in Table 1. These method vary in choice of chemical reaction and way of computing the set of non-linear equations (Kozaczka, 1994).

When analyzing models shown in Table 1, two issues should be taken into account:

- Most of the presented methods originally had iterative character. Nowadays, by using various software (unnecessarily dedicated) the solution may be easily found in one step,
- Some methods presented in the table do not include the composition of fuel, consequently for each coal the results are the same. In the opinion of the author of this article, it will be better to apply the extended versions of these methods (or completely different models), which take into consideration coal properties. The comparison of the exemplary original model (the three points method by Traustel) and their extension (by Gumz) is given in Table 2. In order to show discrepancies between these models, relative errors were calculated (where results from the extended model were used as values of reference). It could easily be seen that differences between the aforementioned methods are significant (especially for nitrogen), however results for coal with a higher content of element C (sample 1) are slightly more similar for both models⁴.

3.2. Non-stoichiometric model

The non-stoichiometric model of gasification requires the definition of the following inputs:

- the parameters of the process (pressure and temperature),
- the initial composition of the reacting mixture,
- the set of chemical compounds taking part in the process,
- the set of expressions defining the thermodynamic potential of each species (Tabiś, 2002).

Aiming for equilibrium, Gibbs free energy of system declines, reaching its minimum in this state $G^t = \min$. The total Gibbs free energy of the system can be calculated using the equation:

$$G^t = \sum_{i=1}^n n_i \mu_i \quad (15)$$

Because the chemical potential of the species i (μ_i) is defined as:

$$\mu_i = \Delta_R G_{i,298}^\circ + RT \ln(x_i) \quad (16)$$

² Where v_i is stoichiometric coefficient of reactant i in chemical reaction.

³ Extent of reaction ξ is defined as $\xi = \frac{\Delta n_i}{v_i} = \frac{n_{0i} - n_i}{v_i}$.

⁴ Therefore the use of methods which do not include fuel composition may be optionally justified for high ranked coals.

Table 1. Review of engineering methods of calculating equilibrium gasification processes – own elaboration based on (Kozaczka, 1994)

Method	Syngas composition	Input parameters	Included reactions	Solution method	Remarks
method by Deringer	CO, CO ₂ , N ₂ , H ₂ O, H ₂ , CH ₄	T, p, composition of gasifying agent	(a), (b), (c)	estimation that value of unknown x ($x = \frac{n_{CO}}{n_{H_2}}$), which permits to obtain equality $K_a = K_b$, where:	- composition of fuel is not included
method by Deringer and Traustel	CO, CO ₂ , N ₂ , H ₂ O, H ₂ , CH ₄	T, p, composition of gasifying agent, fuel composition	(a), (c), (d)	K_a – equilibrium constant calculated from fractions of gas components (determined by using unknown x), K_b – equilibrium constant at a given temperature	- any composition of fuel - balance of element H is uncertain for small amount of H ₂ O in system
method by Gumz	CO, CO ₂ , N ₂ , H ₂ O, H ₂ , CH ₄ , H ₂ S, COS	T, p, composition of gasifying agent, fuel composition	(a), (c), (d), (e), (f)		- including sulfur compounds - any composition of fuel
three points method by Traustel	CO, CO ₂ , N ₂ , H ₂ O, H ₂ , CH ₄	T, p, composition of gasifying agent	(a), (b), (c)	estimation that values of $x = P_{CO}$, $y = P_{H_2}$, which permit to obtain the partial pressure of gas components satisfying the determined criterion equations	- composition of fuel is not included - using values of x and y form previous series of calculation does not ensure convergence
three points method by Traustel – extension by Gumz	CO, CO ₂ , N ₂ , H ₂ O, H ₂ , CH ₄	T, p, composition of gasifying agent, fuel composition	(a), (b), (c)		- any composition of fuel - using values of x and y form previous series of calculation does not ensure convergence
Newtonian approximation by Gumz	CO, CO ₂ , N ₂ , H ₂ O, H ₂ , CH ₄ , H ₂ S, COS, S ₂ , CS ₂	T, p, composition of gasifying agent, fuel composition	(a), (b), (c), (e), (f), (g), (h)	estimation that values of x_{CO} , x_{H_2} , x_{H_2S} , which permit to obtain fractions of gas components satisfying the determined criterion equations determination of syngas composition based on the definition of reaction yield (initially estimated for each reaction) so as to obtain equality $K_b = K_c$	- any composition of fuel - composition of fuel is not included - method is not very effective
method by Zeise-Gumz	CO, CO ₂ , N ₂ , H ₂ O, H ₂ , (CH ₄)	T, p, composition of gasifying agent	(b), (c), (d)		- any composition of fuel - method is not very effective or dependable - method permits to determine temperature above which the system is homogenous
method by Grumbt	CO, CO ₂ , N ₂ , H ₂ O, H ₂ , CH ₄	p, composition of gasifying agent, fuel composition	(a), (b), (c), (d)	estimation of temperature T_c , above which carbon does not occur (theoretically) in the solid phase	
method by Samsel	CO, CO ₂ , N ₂ , H ₂ O, H ₂ , CH ₄	T, p, composition of gasifying agent, fuel composition, value of ω^*	(a), (c), (d)	estimation of value of unknown x ($x = \frac{n_{CO_2}}{n_{CO}}$) so as to obtain (after series of calculations) convergence to some number	- generation of soot is included - any composition of fuel
method by Rumler-Göhler	CO, CO ₂ , N ₂ , H ₂ O, H ₂ , CH ₄	T, p, composition of gasifying agent, fuel composition	(a), (b), (c), (d)	estimation of value of unknown x_{CH_4} , which permits to obtain equality $K_{c/b} = K_{c/b}$, where $K_{c/b}$ – equilibrium constant calculated from fractions of the gas components (determined by using unknown x), $K_{c/b}$ – equilibrium constant at a given temperature	- any composition of fuel
method by Dolch	CO, CO ₂ , H ₂ O, H ₂ , (N ₂)	T, p, composition of gasifying agent	(a), (d)	solution of cubic equation (for unknown n_{CO})	- the simplest method (can be used in initial analysis) - generation of CH ₄ is not included - composition of fuel is not included
(a) C + CO ₂ → 2CO		(e) 0.5S ₂ + H ₂ → H ₂ S			
(b) C + H ₂ O → CO + H ₂		(f) 0.5S ₂ + CO → COS			
(c) C + 2H ₂ → CH ₄		(g) S ₂ + C → CS ₂			
(d) CO + H ₂ O → CO ₂ + H ₂		(h) 2CO + SO ₂ → 2CO ₂ + 0.5S ₂			

* ω – ratio of actual amount of injected air to theoretical amount of air, required in process

Table 2. Result of simulations (obtained with the three points method of Traustel and their extended version by Gumz) carried out for two coals, at a temperature equal to 600, 800, 1000, 1200°C (own elaboration)

Component	Coal 1*			Coal 2**		
	component mole fraction (original method)	component mole fraction (extended method)	relative error [%]	component mole fraction (original method)	component mole fraction (extended method)	relative error [%]
<i>T</i> = 600°C						
CO	0.121162	0.117733	2.912522	0.121162	0.122339	0.962081
H ₂	0.223943	0.274222	18.33514	0.223943	0.289503	22.64571
CO ₂	0.154993	0.146342	5.911495	0.154993	0.158017	1.913718
H ₂ O	0.1122	0.133501	15.95569	0.1122	0.146455	23.38944
CH ₄	0.0232486	0.0348599	33.30847	0.0232486	0.0388534	40.16328
N ₂	0.364453	0.293343	24.24125	0.364453	0.244833	48.85779
<i>T</i> = 800°C						
CO	0.351073	0.360796	2.694875	0.351073	0.391081	10.23011
H ₂	0.260164	0.38076	31.67244	0.260164	0.415021	37.31305
CO ₂	0.0161192	0.0170244	5.317074	0.0161192	0.0200024	19.41367
H ₂ O	0.011462	0.0172396	33.51354	0.011462	0.0203681	43.72573
CH ₄	0.0031917	0.00683642	53.31328	0.0031917	0.00812208	60.70342
N ₂	0.35799	0.217344	64.71124	0.35799	0.145406	146.2003
<i>T</i> = 1000°C						
CO	0.375791	0.39088	3.860264	0.375791	0.427376	12.07017
H ₂	0.264302	0.397404	33.49287	0.264302	0.43572	39.34132
CO ₂	0.000942176	0.00101936	7.57181	0.000942176	0.00121859	22.6831
H ₂ O	0.00114401	0.0017892	36.06025	0.00114401	0.00214486	46.66272
CH ₄	0.000664126	0.00150146	55.76799	0.000664126	0.00180495	63.2053
N ₂	0.357157	0.207406	72.20186	0.357157	0.131736	171.1157
<i>T</i> = 1200°C						
CO	0.376965	0.392661	3.997341	0.376965	0.429487	12.22901
H ₂	0.265155	0.399848	33.68605	0.265155	0.438636	39.55011
CO ₂	0.000111653	0.000121144	7.834478	0.000111653	0.000144933	22.96233
H ₂ O	0.000202933	0.000318761	36.33694	0.000202933	0.000382478	46.94257
CH ₄	0.000205555	0.000467434	56.02481	0.000205555	0.00056252	63.45819
N ₂	0.35736	0.206584	72.98532	0.35736	0.130787	173.2382

* composition of coal 1 (analytical): C = 83.8%, S = 0.28%, H = 4.9%, N = 1.2%, O = 6.12%, moisture = 1.5 %, ash = 2.2%, (Stańczyk et al., 2011),

** composition of coal 2 (analytical): C = 50.7%, S = 1.9%, H = 3.9%, N = 1.3%, O = 19.1%, moisture = 14.5%, ash = 8.6%, (Stańczyk et al., 2011).

(where $\Delta_R G_{i,298}^\circ$ is standard Gibbs free energy of formation of species *i*), the total Gibbs free energy of the system can be determined from the equation:

$$G^t = \sum_{i=1}^n n_i \Delta_R G_{i,298}^\circ + \sum_{i=1}^n n_i R T \ln \left(\frac{n_i}{n} \right) \quad (17)$$

Now, the problem is reduced to finding the number of moles of each species which minimize expression (17). Lagrange multipliers can be used to this purpose¹ (Jarungthamachote & Dutta, 2008).

For the reason that elemental balances are constraints in the analyzed problem of minimized Gibbs free energy:

$$\sum_{i=1}^N a_{ij} n_i = A_j \quad (18)$$

where:

a_{ij} – number of atoms of element *j* in compound *i* [-];

A_j – total number of atoms of element *j* in reacting mixture [-],

Lagrangian function is defined as:

$$L = G^t - \sum_{j=1}^k \lambda_j \left(\sum_{i=1}^N a_{ij} n_i - A_j \right) \quad (19)$$

From constraints (18) and expressions $\left(\frac{\partial L}{\partial x_i} \right) = 0$ a set of

equations can be formed. The number of moles of each species n_i are the solution for this set of equations (Jarungthamachote & Dutta, 2008).

4. MODEL ANALYSIS

Equilibrium models are valuable tools for the prediction of thermodynamic limits of the gasification process proceeding in reactors, which work in high temperatures or by an appropriate length of time. These kinds of models are also computationally easy and converge quickly. Equilibrium calculations are available in many common codes dedicated to the simulation of chemical installations (Aspen Plus or ChemCad), but also can be implemented to commercial computation programs like Mathematica (Golec & Ilmurzyńska, 2008).

On the other hand equilibrium models are zero-dimensional – the geometry of the reactor is not considered. A uniform temperature is assumed in the whole reactor; oxidation, reduction and drying and the pyrolysis zone are taken

¹ Method of Lagrange multipliers permits to determine conditional extremum of function of several variables $f(X) = f(x_1, x_2, \dots, x_k)$ when *m* constraints are given: $\varphi_j(X) = 0$ ($j = 1, 2, \dots, m$). Providing that Lagrangian function is defined as:

$$F(x_1, x_2, \dots, x_k, \lambda_1, \lambda_2, \dots, \lambda_m) = f(X) + \lambda_1 \varphi_1(X) + \lambda_2 \varphi_2(X) + \dots + \lambda_m \varphi_m(X),$$

where $\lambda_1, \lambda_2, \dots, \lambda_m$, are Lagrange multipliers, conditional extremum of function *F* can be determined from following set of equation:

$$\begin{cases} \frac{\partial F}{\partial x_i} = 0 & i = 1, 2, \dots, k \\ \varphi_j = 0 & j = 1, 2, \dots, m \end{cases} \quad (\text{Grzymkowski, 2000})$$

into account as one zone². Moreover, in these kinds of models heat losses are often neglected (the reactor is considered to be perfectly insulated) and tar formation is not simulated (Puig-Arnavat, Bruno, & Coronas, 2010). Neglecting heat exchange in simulations between reacting system and its surroundings may lead to the calculation of better results than results obtained in real reactors. It is especially seen in the case of gasification carried in a steam environment. Reaction (3) is strongly endothermic and requires continuous heat delivery to the reactor (otherwise it results in a reduction of temperature in the reacting system).

The most significant disadvantage of thermodynamic models is the assumption of a state of equilibrium. This condition is not always accurate in low temperatures or for too short residence time. Furthermore, values of equilibrium constants given in different studies are not uniform – they may vary even in a couple of orders of magnitude (Table 3). Approximated equations determining equilibrium constants also may take various forms (Kozaczka, 1994).

Table 3. Values of equilibrium constant from different studies

Reaction	800°C	1000°C	1200°C	1400°C
C+CO ₂ ↔2CO	7.08525 *	1.39799·10 ² *	1.19846·10 ³ *	6.05341·10 ³ *
	7.64633 **	1.49886·10 ² **	1.2727·10 ³ **	6.3463·10 ³ **
	6.430 ***	1.168·10 ² ***	8.976·10 ² ***	3.956·10 ³ ***
C+H ₂ O↔CO+H ₂	7.05095 *	7.81276·10 ¹ *	4.50631·10 ² *	1.71339·10 ³ *
	7.9688 **	8.6826·10 ¹ **	4.925·10 ² **	1.8707·10 ³ **
	6.986 ***	7.074·10 ¹ ***	3.638·10 ² ***	1.201·10 ³ ***
C+2H ₂ ↔CH ₄	4.72172·10 ⁻² *	9.43927·10 ⁻³ *	2.89534·10 ⁻³ *	1.18357·10 ⁻³ *
	4.7156·10 ⁻² **	9.5072·10 ⁻³ **	2.0305·10 ⁻³ **	1.1998·10 ⁻³ **
	4.248·10 ⁻² ***	8.027·10 ⁻³ ***	2.263·10 ⁻³ ***	8.252·10 ⁻⁴ ***
CO ₂ +H ₂ ↔CO+H ₂ O	1.00486 *	1.78937 *	2.65953 *	3.533 *
	0.95954 **	1.72624 **	2.58422 **	3.39248 **
	0.919963 ***	1.65098 ***	2.46731 ***	3.29381 ***

* – precise calculations based on equations (6)–(10) and thermodynamic data from work (Kozaczka, 1994),

** – calculations based on approximated equations by Gumz, given in work (Kozaczka, 1994),

*** – equilibrium constants given in work (Pérez-Fortes & Bojarski, 2011).

A slight drop (or rise) in temperature causes considerable changes of the equilibrium constant value (Fig. 1), which is the reason behind significant deviations in fractions of syngas species. It should also be underlined that values of equilibrium constants and approximated equations have been obtained from experiments, which in heat conditions may be different than those occurring in real reactors (Kozaczka, 1994).

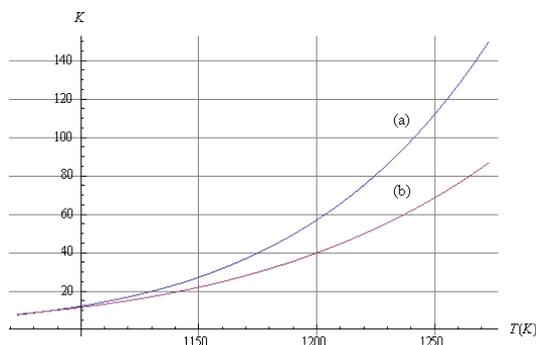


Figure 1. Values of equilibrium constant of reaction $C + CO_2 \rightarrow 2CO$ (a) and reaction $C + H_2O \rightarrow CO + H_2$ (b) at different temperatures

² In the case of UCG reactors with a strongly zonal character (where temperatures in particular zones are significantly different) this assumption may generate errors. As a result of equilibrium simulation, uniform gas is obtained for the whole gasifying channel, while in real reactors in the oxidation, reduction and drying and pyrolysis zone different compositions of product are observed.

It is also assumed in equilibrium models that the analyzed gases are considered to be ideal gases. This presumption is correct only in conditions of low pressure, near to atmospheric pressure. As the pressure rises, the value of the equilibrium constant, calculated for ideal gases, becomes increasingly different from real equilibrium constant (Table 4). In this situation, the fugacity of each compound of the reacting mixture should be taken into account.

Table 4. Values of the equilibrium constant of reaction $CO_2 + H_2 \rightarrow CO + H_2O$ in temperature 673 K for real gases in different pressures (Kozaczka, 1994)

p [atm.]	K _p
10	0.096
60	0.106
80	0.109
100	0.112

5. CONCLUDING REMARKS

1. There are two general approaches applied in the equilibrium modeling of coal gasification – stoichiometric and non-stoichiometric. Both of them give the same results, but stoichiometric procedure is mathematically easier and converges faster. Therefore many engineering calculation methods, shortly presented in this paper, are based on this approach. These methods vary in the number of included reactions, required input data and methodology of searching results.
2. Equilibrium simulations are useful in the preliminary analysis and optimization of the coal gasification process because of simple mathematical formulation and the short time required for computation (in comparison to other approaches, especially CFD). Results obtained in equilibrium calculations may act as a point of reference for more complex simulations. These kinds of models can also lead to a better understanding of thermodynamic mechanisms which rule gasification. For example, equilibrium models are valuable tools for the simple determination of the influence of various factors (temperature, pressure, kind of gasifying medium etc.) on syngas composition.
3. A UCG reactor shows zonal character (as the moving bed reactor in case of surface processes), with different temperatures in particular zones. Therefore the perfect mixing and uniform temperature assumed in equilibrium simulations may lead to errors.
4. The determination of equilibrium parameters for the purpose of carrying out calculations may be problematic – equilibrium constants and approximated equations given in literature may, not only, significantly differ, but also are connected with simplistic assumptions, for example gases are treated as ideal.
5. Another problem appears when a reactor is treated as perfectly insulated. Some reactions are strongly endothermic (especially water gas reaction) what may lead to the reduction of temperature in the system. Many equilibrium models do not take this issue into consideration, therefore results obtained from them are more optimistic than results from experimental procedures.
6. An equilibrium model cannot be applied for processes which are proceeding very quickly, in a transient state, low temperature and when it is necessary to include in

simulations some physical phenomena, like for example turbulent mixing. In these situations more advanced kinetic and CFD models should be used (critical analysis of these models will be undertaken in Part II of these paper).

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