REVIEW PAPER

CRITICAL ANALYSIS OF UNDERGROUND COAL GASIFICATION MODELS. PART II: KINETIC AND COMPUTATIONAL FLUID DYNAMICS MODELS

Alina Żogała

Interdisciplinary PhD Studies in the Field of Clean Coal Technologies, Central Mining Institute (Katowice, Poland)
Corresponding author: e-mail: azogala@autograf.pl, tel.: +48 503 161 360

ABSTRACT

Purpose	Underground coal gasification, as a complex and technically difficult process, in many aspects requires the support provided by computer simulations. There are a lot of mathematical models of UCG, some of them are concentrated with the forecast of syngas composition. The most important may be divided into three groups: equilibrium, kinetic and CFD models. The purpose of this work was the detailed critical analysis of more advanced approaches (than equilibrium considerations) applied in simulations of the coal conversion process – both kinetic and based on computational fluid dynamics. The other aim of this paper was the comparative analysis of the most important models of underground coal gasification.
Methods	Literary studies, concerned with the features and mathematical description of kinetic and CFD models of coal gasification, were used as the research method applied in the work presented. Compilation of the kinetic parameters of gasification reactions was an important part of this article. For that purpose the analysis of Polish and foreign papers, monographs and university handbooks was undertaken.
Results	Critical analysis of kinetic and CFD models of coal gasification (together with their mathematical formulation) was the result of considerations presented in this article. Kinetic equations were shown separately for pyrolysis, homogenous and heterogeneous reactions. In the case of CDF models, except for the presentation of the conservation equation, the most important methods of modeling turbulence are described (for the reason that this phenomenon may have significant influence on the final results).
Practical implications	The work presented describes practical issues connected with kinetic and CFD models, focusing on their capabilities, drawbacks and possible application problems.
Originality/value	This paper presents state of art in the field of coal gasification modeling using kinetic and computational fluid dynamics approach. The paper also presents own comparative analysis (concerned with mathematical formulation, input data and parameters, basic assumptions, obtained results etc.) of the most important models of underground coal gasification.

Keywords
coal gasification, kinetic models, CFD models

1. INTRODUCTION

Underground coal gasification is a difficult process owing to a variety of phenomena occurring in the reactor, changes of the parameters over time and space and the ambiguous characteristics of coal (Golec & Ilmurzyńska, 2008). In these situations mathematical models are valuable tools which support the theoretical analysis of the process and enable its optimization in order to obtain syngas with determined chemical composition and maximal heat value (Wachowicz, Janoszek, & Iwaszenko, 2010).

There are a lot of UCG models, concentrated on the prediction of syngas composition, which can be divided into equilibrium, kinetic and CFD (*Computational Fluid Dynamics*) models (Golec & Ilmurzyńska, 2008). Kinetic and CFD models are analyzed in this article. The equilibrium approach was presented in Part I of this paper.

2. KINETIC MODEL

Kinetic models consider the progress of chemical reactions over time. They are based on kinetic equations – relationships between temperature, the concentrations of reactants and the rates of chemical reactions (which determine changes of the concentrations of the species over time). When the expression of the kinetic equation is known, the composition of the re-

acting mixture can be computed in a selected stage of the process (Tabiś, 2000; Atkins, 2001).

2.1. Kinetics of homogenous reactions

Generally, the kinetic equation for the chosen chemical reaction is given by the expression:

$$r = \pm \frac{dC_i}{dt} = k(T)f(C) \tag{1}$$

where:

r – rate of chemical reaction, $kmol/m^3 \cdot s$;
C_i – molar concentration of species **i**, $kmol/m^3$;
t – time, s;
$k(T)$ – kinetic constant of forward reaction (depending on temperature), vary units;
$f(C)$ – function depending on concentrations of reactants, vary units.

The rate of irreversible reaction is defined as:

$$r = k_1(T) \prod_i C_{S,i}^{a_i} \tag{2}$$

where:

a_i – rate exponent of substrate **i** [-];
$C_{S,i}$ – molar concentration of substrate **i**, $kmol/m^3$;
k_1 – rate constant of forward reaction, vary units.

The rate of reversible reaction is determined by the expression:

$$r = k_1(T) \prod_i C_{S,i}^{a_i} - k_2(T) \prod_i C_{P,i}^{b_i} \tag{3}$$

where:

b_i – rate exponent of product **i** [-];
$C_{P,i}$ – molar concentration of product **i**, $kmol/m^3$;
k_2 – rate constant of backward reaction, which may be computed as: $k_2 = \dfrac{k_1}{K_p}$.

The rate constant of reaction k_1 is calculated using the Arhenius expression (Tabiś, 2000; Atkins, 2001):

$$k_1 = AT^B e^{-E/RT} \tag{4}$$

where:

A – pre-exponential factor, vary units;
B – temperature exponent [-];
E – activation energy, kJ/kmol;
R – universal gas constant, kJ/kmol·K.

2.2. Devolatilization models

Pyrolysis (devolatilization), the initial step of most coal conversion processes, is the decomposition of fuel due to the effect of temperature, in the absence of air, oxygen or other oxidizers. Many substances are formed in the pyrolysis process: gases (CO, H_2, CH_4, H_2O), water, liquid hydrocarbons (tar, oil, naphtha) and solid char. The amount and composition of these products depend on the properties of the fuel and the parameters of the process (Bhutto, Bazmi, & Zahedi, 2013; Golec & Ilmurzyńska, 2008).

There are many coal devolatilization models in literature. In the simplest approach, the Arheniuss equation links the rate of process with temperature; pyrolysis is considered to be a single reaction or a combination of parallel reactions. These reactions are typically treated as first order reactions (Gómez-Barea & Leckner, 2010).

The Single First Order Reaction model represents pyrolysis kinetics as (Bhutto et al., 2013):

$$\frac{dV}{dt} = k_r(V^* - V) \tag{5}$$

where:

V – released amount of volatiles at time t, m^3;
V^* – initial amount of volatiles in coal, m^3;
or by the expression:

$$coal \xrightarrow{k_1} Y \cdot volatiles + (1-Y) \cdot char \tag{6}$$

where Y – volatile fraction, representing partitioning of coal into char and volatiles (Williams, Pourkashanian, & Jones, 2001).

A two-step devolatization model includes two reactions:

$$coal \xrightarrow{k_1} Y_1 \cdot volatiles + (1-Y_1) \cdot char_1 \tag{7}$$

$$coal \xrightarrow{k_2} Y_2 \cdot volatiles + (1-Y_2) \cdot char_2{}^1 \tag{8}$$

Reaction (7) is dominant when the temperature is relatively low. If the temperature is relatively high, reaction (8) is predominant (Williams et. al., 2001; Chen, Hung, & Chen, 2012).

In general, case pyrolysis is determined as (Bhutto et al., 2013):

$$\frac{dV_i}{dt} = k_{i,r}(V_i^* - V_i) \tag{9}$$

where:

V_i^* – initial amount of species **i** in coal, m^3;
V_i – released amount of species **i** from coal, m^3.

2.3. Gas-solid reaction kinetic models

Reactions between the gasifying agent and char are a limiting stage of gasification (because they are much slower than the processes of pyrolysis). The shape, size and structure of the char particle are changing during these reactions, which affects the transport of mass, momentum and energy and consequently has an effect on the rate of process. If chemical reaction is associated with generating gradients of temperature it can also change the rate of gasification (Golec & Ilmurzyńska, 2008).

Kinetic of gas-solid reaction is given by the equation:

$$\frac{dX}{dt} = kf(X) \tag{10}$$

where:

k – rate of reaction related to unit of grain surface, 1/s;
X – fractional char conversion [-];
$f(X)$ – function describing changes of char structure during gasification [-].

Fractional char conversion is determined as:

$$X = \frac{W_0 - W(t)}{W_0 - W_{ash}} \tag{11}$$

where:

W_0 – initial weight of char, kg;
$W_{(t)}$ – weight of char at time t, kg;
W_{ash} – weight of ash in char, kg.

---

[1] Rate constants k_r, k_1 and k_2 are determined from Arheniuss equation.

The formulation of function $f(X)$ depends on kinetic model of gas-solid reaction used. The most important of them are given in Table 1 (Gómez-Barea & Leckner, 2010; Chaiyot, Supunnee, & Juejun, 2013).

Table 1. Main kinetic models of gas-solid reaction (Gómez-Barea & Leckner, 2010; Chaiyot et al., 2013)

Model	Model assumption	Rate equation
volume reaction model (VRM)	homogenous reaction of char particle	$\dfrac{dX}{dt} = k(1-X)$
shrinking core model (SCM)	core of nonporous grain shrinks during reaction	$\dfrac{dX}{dt} = k(1-X)^{2/3}$
random pore model (RPM)	structure of pores changes during reaction	$\dfrac{dX}{dt} = k(1-X)[1-\Psi\ln(1-X)]^{1/2}$
modified volume reaction model (MVRM)	value of k changes during reaction	$\dfrac{dX}{dt} = k(X)(1-X)$

The volume reaction model assumes that the reaction proceeds steadily in the whole volume of grain. There are no gradients of concentrations inside the particle. The gasifying medium reacts with carbon at the same rate, irrespective of position in the particle (Golec & Ilmurzyńska, 2008).

The shrinking unreacted core model and shrinking unreacted particle model describe a case of a dense, non-porous char particle, where reaction occurs on the surface and moves across to the interior of the grain (Golec & Ilmurzyńska, 2008; Gómez-Barea & Leckner, 2010). This process is associated with ash production. In the shrinking unreacted core model ash covers the surface of the particle. The radius of the core decreases during reaction but particle size is still the same, because the ash layer grows. In the shrinking unreacted particle model ash is removed from the reaction zone and consequently the dimension of the grain decreases. Both model are determined by the same kinetic equation – second position in table 1 (Gómez-Barea & Leckner, 2010).

The aforementioned models have extended versions – called progressive models (PM), where the reaction proceeds in the whole particle and intermediate states occur. Ash is removed or remains in the reaction zone. PM models are computationally more difficult than SCM models. The specification of these models (and VRM) is given in Table 2 (Gómez-Barea & Leckner, 2010).

Table 2. Main char-particle conversion models (Gómez-Barea & Leckner, 2010)

Model	Scheme
volume reaction model (VRM)	Time
shrinking unreacted particle model (SUPM)	Time
shrinking unreacted core model (SUCM)	Time
progressive model with shrinking reacting particle (PMSP)	Time
progressive model with shrinking reacting core (PMSC)	Time
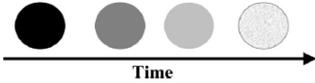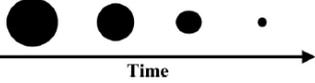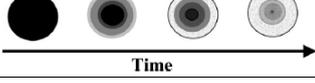
The random pore model describes porous particle, whose interior surface changes during the reaction progress. This model contains parameter Ψ – dimensionless coefficient of char structure, given by the expression:

$$\Psi = 4\pi L_0 (1-\varepsilon_0)/S_0^2 \tag{12}$$

where:
ε_0 – initial porosity [-];
L_0 – initial total length of pores related to volume unit, $1/m^2$;
S_0 – initial surface of grain related to volume unit, $1/m$.

The huge value of parameter Ψ means that the initial porosity of the grain is small and changes in the interior surface have a significant influence on the reaction rate (Golec & Ilmurzyńska, 2008).

2.4. Model analysis

Kinetic models are a solution in situations where the thermodynamic approach cannot be used – when time of process is too short and temperature too low to ensure equilibrium state (Pèrez-Fortes & Bojarski, 2011). They also give information about reaction mechanisms, intermediate states and show how different conditions of a process influence on the rate of chemical reactions (Bhutto et al., 2013). Kinetic models operate in a transient state, therefore parameters of gasification can be determined for a chosen time of the process (Golec & Ilmurzyńska, 2008). In the opinion of the author of this article, a kinetic approach better models a UCG reactor than an equilibrium one. The gasification process proceeds over a relatively long period of time (in comparison, for example, to an entrained flow reactor), therefore its parameters change over time and this fact should be included in the model (which kinetic simulations ensure)[2].

On the other hand, simulations based on the kinetic approach are computationally more difficult than equilibrium ones – they consist of sets of ordinary differential equations with initial conditions (concentrations of components at the first moment of the process). Nevertheless, there is a great deal of appropriate software to solve this problem, such as Mathematica or the ordinary differential equation (ODE) toolbox in Matlab (Ahmed, Ahmad, Yusup, Inayat, & Khan, 2012).

Significant differences in kinetic parameters (activation energies and pre-exponential factors) given in literature are the most considerable problem connected with kinetic models. Kinetic parameters of the main reactions from different studies are collected in Table 3[3]. Additionally, different values of k of the Bourdouard reaction as a function of temperature are presented in Figure 1. These parameters are obtained in an experimental way and may be valid only for the determined condition of the process or type of coal (Łabojko, Morańska-Kotyczka, Plis, & Ściążko, 2012). Therefore the author of the current article recommends using (if it is possible) kinetic parameters from one reference.

---

[2] Nevertheless kinetic model posses the one same problem as equilibrium one – assumption of uniform temperature in whole reactor (what was indicated in part I of this article).

[3] Dimensionless parameter B (temperature exponent) was also included in table. In most cases it is assumed that temperature exponent equal is to 0, but some authors give another value of this parameter.

Table 3. Parameters of chemical kinetics from different studies[1]

Reaction	A	B [-]	E [J/kmol]	References
$C + 0.5O_2 \rightarrow CO$	0.002 (m$^{1.5}$kmol$^{-0.5}$s^{-1})	0	$7.9 \cdot 10^7$	Chen et al., 2012
	$8.55 \cdot 10^4$ (m$^{1.5}$K$^{-0.84}$kmol$^{-0.5}$s^{-1})	0.84	$1.4 \cdot 10^8$	Watanabe & Otaka, 2006
	3.3 (m s^{-1})	0	$6.113 \cdot 10^7$	Silaen & Wang 2010
	0.052 (kg m^{-2}Pa$^{-0.5}$s^{-1})	0	$1.33 \cdot 10^7$	Silaen & Wang 2009
$(2C + O_2 \rightarrow 2CO)$	$1.813 \cdot 10^3$ (m s^{-1})	0	$1.089 \cdot 10^8$	Li, Wei, & Jin, 2003
	$1.2 \cdot 10^4$ (s^{-1})	0	$1.18 \cdot 10^8$	Boiko & Pachkovskii, 2004
$C + CO_2 \rightarrow 2CO$	242 (m^{3}kmol^{-1}s^{-1})	0	$2.75 \cdot 10^8$	Chen et al., 2012
	$8.55 \cdot 10^4$ (m^{3}K$^{-0.84}$kmol^{-1}s^{-1})	0.84	$1.4 \cdot 10^8$	Watanabe & Otaka, 2006
	4.4 (m^{3}K^{-1}kmol^{-1}s^{-1})	1	$1.62 \cdot 10^8$	Silaen & Wang, 2010
	$7.375 \cdot 10^3$ (m s^{-1})	0	$1.380 \cdot 10^8$	Li et al., 2003
	$6.94 \cdot 10^4$ (m s^{-1})	0	$1.854 \cdot 10^8$	Tomeczek, 1992
	0.0732 (kg m^{-2}Pa$^{-0.5}$s^{-1})	0	$1.125 \cdot 10^8$	Silaen & Wang 2009
	$79.0 \cdot 10^4$ (s^{-1})	0	$2.14 \cdot 10^8$	Boiko & Pachkovskii, 2004
$C + H_2O \rightarrow CO + H_2$	426 (m^{3}kmol^{-1}s^{-1})	0	$3.16 \cdot 10^8$	Chen et al., 2012
	$8.55 \cdot 10^4$ (m^{3}K$^{-0.84}$kmol^{-1}s^{-1})	0.84	$1.4 \cdot 10^8$	Watanabe & Otaka, 2006
	1.33 (m^{3}K^{-1}kmol^{-1}s^{-1})	1	$1.47 \cdot 10^8$	Silaen & Wang, 2010
	$5.96 \cdot 10^4$ (m s^{-1})	0	$2.083 \cdot 10^8$	Tomeczek, 1992
	0.0782 (kg m^{-2}Pa$^{-0.5}$s^{-1})	0	$1.15 \cdot 10^8$	Silaen & Wang, 2009
	$1.6 \cdot 10^4$ (s^{-1})	0	$1.814 \cdot 10^8$	Boiko & Pachkovskii, 2004
$H_2 + 0.5O_2 \rightarrow H_2O$	$5 \cdot 10^{10}$ (m$^{1.5}$kmol$^{-0.5}$s^{-1})	0	$1.68 \cdot 10^8$	Chen et al., 2012
	$6.8 \cdot 10^{15}$ (m^{3}K^{-1}kmol^{-1}s^{-1})	0	$1.68 \cdot 10^8$	Watanabe & Otaka, 2006
	$1.5 \cdot 10^{13}$ (m$^{4.5}$kmol$^{-1.5}$s^{-1})	0	$2.85 \cdot 10^7$	Tomeczek, 1992
$(2H_2 + O_2 \rightarrow 2H_2O)$	250 (s^{-1})	0	$4.11 \cdot 10^7$	Boiko & Pachkovskii, 2004
$CO + 0.5O_2 \rightarrow CO_2$	$2.2 \cdot 10^{20}$ (m$^{1.5}$kmol$^{-0.5}$s^{-1})	0	$1.67 \cdot 10^7$	Chen et al., 2012
	$2.2 \cdot 10^{12}$ (m$^{1.5}$kmol$^{-0.5}$s^{-1})	0	$1.67 \cdot 10^8$	Watanabe & Otaka, 2006
	$2.2 \cdot 10^{12}$ (m$^{1.5}$kmol$^{-0.5}$s^{-1})	0	$1.67 \cdot 10^8$	Silaen & Wang, 2010
	$1.1 \cdot 10^{10}$ (m$^{2.25}$kmol$^{-0.75}$s^{-1})	-0.75	$1.33 \cdot 10^8$	Tomeczek, 1992
$(2CO + O_2 \rightarrow 2CO_2)$	$7.0 \cdot 10^4$ (m^{3}kg^{-1}s^{-1})	0	$6.651 \cdot 10^7$	Li et al., 2003
	220 (s^{-1})	0	$4.27 \cdot 10^7$	Boiko & Pachkovskii, 2004
$CO + H_2O \rightarrow CO_2 + H_2$	$2.6 \cdot 10^{10}$ (m^{3}kmol^{-1}s^{-1})	0	$8.4 \cdot 10^8$	Chen et al., 2012
	$2.75 \cdot 10^{10}$ (m^{3}kmol^{-1}s^{-1})	0	$8.38 \cdot 10^7$	Watanabe & Otaka, 2006
	$2.75 \cdot 10^2$ (m^{3}kmol^{-1}s^{-1})	0	$8.38 \cdot 10^7$	Silaen & Wang, 2010
	$4.2 \cdot 10^7$ (s^{-1})	0	$1.383 \cdot 10^8$	Boiko & Pachkovskii, 2004
$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$	4000 (m$^{1.5}$kmol$^{-0.5}$s^{-1})	-1	$1.26 \cdot 10^6$	Chen et al., 2012
	$3.0 \cdot 10^8$ (m$^{1.5}$K^{-1}kmol$^{-0.5}$s^{-1})	-1	$1.26 \cdot 10^8$	Watanabe & Otaka, 2006
$CH_4 + H_2O \rightarrow CO + 3H_2$	4400 (m^{3}kmol^{-1}s^{-1})	0	$1.68 \cdot 10^8$	Chen et al., 2012
	$4.4 \cdot 10^{11}$ (m^{3}kmol^{-1}s^{-1})	0	$1.68 \cdot 10^8$	Watanabe & Otaka, 2006
$C + O_2 \rightarrow CO_2$	$1.225 \cdot 10^3$ (m s^{-1})	0	$9.977 \cdot 10^7$	Li et al., 2003
	322 (m s^{-1})	0	$9.01 \cdot 10^7$	Tomeczek, 1992
	$1.1 \cdot 10^4$ (s^{-1})	0	$1.13 \cdot 10^8$	Boiko & Pachkovskii, 2004
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	$1.6 \cdot 10^{10}$ (m^{3}kg^{-1}s^{-1})	0	$1.081 \cdot 10^8$	Li et al., 2003
	$1.3 \cdot 10^{12}$ (m^{3}kmol^{-1}s^{-1})	0	$1.305 \cdot 10^8$	Tomeczek, 1992
	230 (s^{-1})	0	$5.03 \cdot 10^7$	Boiko & Pachkovskii, 2004
$C + 2H_2 \rightarrow CH_4$	$0.1 \cdot 10^4$ (s^{-1})	0	$1.131 \cdot 10^8$	Boiko & Pachkovskii, 2004

---

[1] Parameters presented in table of course can not be compared. The aim of author was presentation how many different versions of kinetic equations of one particular reaction exist in literature.
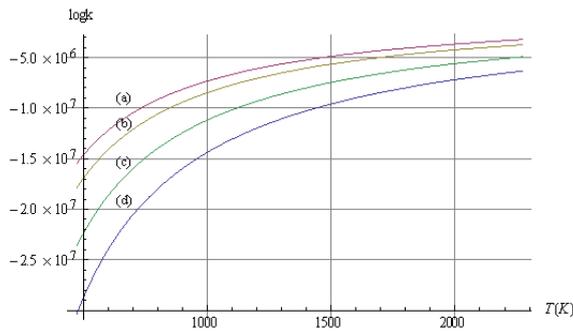
Figure 1. Values of the kinetic constant of the reaction $C + CO_2 \rightarrow 2CO$ as a function of temperature from different studies: (a) Watanabe and Otaka (2006), (b) Silaen and Wang (2010), (c) Boiko and Pachkovskii (2004), (d) Chen et al. (2012)

Structure of kinetic equation is also a result of laboratory tests, and generally it could not be based on the stoichiometry of reaction. Convergence between a kinetic model and stoichiometry, if it occurs, is incidental (Atkins, 2001). Therefore, in most kinetic expressions, the exponents of species' concentrations are not equal to the appropriate stoichiometric coefficients. Moreover, some equations can contain concentrations of species which do not occur the reaction (Gómez-Barea & Leckner, 2010). For example, based on source (Tomeczek, 1992), the rate of reaction:

$$CO + 0.5O_2 \rightarrow CO_2 \tag{13}$$

is given by the expression:

$$r = kC_{CO}C_{O_2}^{0.25}C_{H_2O}^{0.5} \tag{14}$$

In conclusion kinetic models are less general than equilibrium models. However, it does not necessarily have to be a disadvantage – because it may be very useful for design processes with strictly determined parameters.

Particular attention should be paid to pyrolysis models, because simulations of these processes allow for the prediction of the amount of char, gases, tar and another hydrocarbons released in early stages of coal conversion (Williams et al., 2001). Unfortunately, pyrolysis is often not considered in kinetic simulations (for the reason that the number of devolatilization products makes the model too complex) or it is limited to one or two reaction mechanisms (Puig-Arnavat, Bruno, & Coronas, 2010).

The problem of characterizing the volatile amount in coal also occurs in pyrolysis models. The value of V^* is determined using an experimental procedure – usually carried out at a specific temperature, ambient pressure and with a slow heating rate; real conditions of pyrolysis may significantly differ from those. Therefore a kinetic model may give incorrect results. Proximate analysis of fuel is also often not known, therefore coal parameters are estimated using data concerning similar coals. This approach also may lead to errors of modelling (de Souza-Santos, 2004).

3. CFD MODEL

Computational Fluid Dynamics (CFD) is a tool designed for computer simulations of fluid flow, heat and mass transport, chemical reactions and other phenomena connected with these issues, as turbulence (Białecka, 2008). The CDF modeling of gasification requires solving transport equations of mass, momentum, energy and species, with appropriate boundary and initial conditions. As a result of simulation, the spatial distribution of temperature, pressure and species concentration in the reactor is obtained (Białecka, 2008; Jaworski, 2005).

Transport equations are partial differential equations and usually can not be solved analytically – they require numerical methods and discretization of reactor space. Therefore, the solution of the analyzed problem is only an approximate solution, obtained for the chosen point of space and time – nodes of the numerical grid (Jaworski, 2005).

3.1. Basic governing equations

The behavior of fluid is described by conservation equations of mass, momentum, energy and species which are given below (Jaworski, 2005):

- continuity equation:

$$\frac{\partial \rho}{\partial t} + \mathrm{div}(\rho \vec{u}) = S_m \tag{15}$$

- momentum equation:

$$\frac{\partial(\rho \vec{u})}{\partial t} + \mathrm{div}(\rho \vec{u} \vec{u}) = \mathrm{div}(\mu \mathrm{grad}\,\vec{u}) + S_u \tag{16}$$

- energy equation:

$$\frac{\partial(\rho e)}{\partial t} + \mathrm{div}(\rho e \vec{u}) = \mathrm{div}(\lambda \mathrm{grad}\,T - p\vec{u}) + S_e \tag{17}$$

- species transport equation:

$$\frac{\partial(\rho c_\alpha)}{\partial t} + \mathrm{div}(\rho c_\alpha \vec{u}) = \mathrm{div}(\rho D_\alpha \mathrm{grad}\,c_\alpha) + S_\alpha \tag{18}$$

where:

ρ – density of fluid, kg/m^3;
p – pressure, Pa;
$\vec{u}$ – velocity vector of fluid element, m/s;
μ – viscosity of fluid, Pa·s;
e – total energy related to unit mass of fluid, kJ/kg;
λ – thermal conductivity, W/mK;
D_α – diffusion coefficient, m^2/s;
T – temperature, K;
c_α – concentration of species α in mixture, $kmol/m^3$.

The source terms in the equations determined above, associated with the exchange of mass S_m, momentum S_u, energy S_h, and species S_α, in practice occur in specific situations. The mass source term is taken into account in a continuity equation in the presence of discrete phase. The momentum source term is included in the transport equation for flow by porous medium or for discrete phase occurrence. The energy source term is added to conservation equations where radiation heat transfer or heat of reactions are being considered. The source term S_α is related to the changing of concentration of species due to chemical reactions (Ansys Fluent 12.0 Theory Guide, 2009).

3.2. Stages of numerical solution

The solution of the partial differential equation is a process composed of three stages:
- the generation of the numerical grid,
- model discretization,
- the solution of a very large set of algebraic equations.

The creation of the numerical mesh is the first step in partial difference equations' solution– values of unknowns will

be determining in the chosen nodes of this grid (points of space and time). Cells constrained by the wall converging in nodes are the basic elements of the numerical grid. The mesh is determined as structured providing that each node has the same number of neighboring nodes. Otherwise, the grid is characterized as unstructured.

Discretization, the second stage of the numerical solution, is the process of transformation of differential equations to algebraic equations. In a large amount of discretization methods, finite differences (FDM), finite elements (FEM) and finite volumes method (FVM) are undoubtedly the most popular.

The set of algebraic equation is obtained as a result of discretization. Unfortunately, the number of equations is very large (often hundreds of thousands of equations are obtained). Therefore, numerical methods (like Gauss elimination method, Thomas algorithm or Gauss-Seidel method) are required to solve this set of equations (Jaworski, 2005).

3.3. Turbulence models

Turbulence plays an important role in gasification processes – therefore it is often necessary to include the influence of this phenomenon on fluid behavior in simulations. Equations describing turbulent flow are very complex and their direct numerical simulation (DNS) is computationally expensive (every length and time scale of eddies must be resolved – from micrometers to meters in case of gasification analysis) and is reasonable only for small Reynold's numbers ($Re \sim 10^3$–10^4) and simple geometries. Hence, two approaches are used to simulate turbulence effects in fluid flow – Reynolds – averaged Navier-Stokes models (RANS) and Large Eddy Simulations (LES).

In the LES method, transport equations are filtered in a way which permits the direct simulation of large eddies (larger than cell size). Smaller eddies are resolved in a simplified manner by subgrid models. The LES method reduces computational effort in comparison to DNS, which in most of computational power is used to simulate the smallest eddies.

RANS method is based on Reynolds' concept which assumes, that every magnitude ϕ describing turbulent flow is a sum of the time-average component $\overline{\phi}$ and the fluctuating component ϕ' (being a random function of time and space):

$$\phi = \overline{\phi} + \phi' \tag{19}$$

As a result of this conception, additional unknowns (Reynolds stress tensor) occur in set of transport equations, which becomes unclosed and requires the appropriate closure models of turbulence.

Most closure models are based on Boussinesq's hypothesis postulating the definition of turbulent viscosity, which is used to determine Reynolds stress terms. Spalart-Allmaras, *k-ε*, and *k-ω* model are the most popular models in this group. In the second closure conception, called Reynolds Stress Model (RSM), transport equations with stress terms are revolved directly, which makes calculations more accurate but also more computationally expensive (Jaworski, 2005).

3.4. Model analysis

CFD modeling is becoming an increasingly popular technique in the analysis of coal conversion technologies (both combustion and gasification processes). CFD methods describe not only fluid behavior, but also heat and mass transport, turbulence phenomena, chemical reactions, phase changes (melting, vaporization), mechanical movement (e.g. rotating reactors) and pollution formation. Practically, every kind of engineering flow could be analyzed by CFD: laminar, turbulent, compressible, incompressible, single-, two- and multiphase, proceeding in a steady or transient state. Moreover CDF models are three-dimensional models and are capable of simulating very complicated geometries. Therefore CFD models permit the analysis of very complex technological processes, which could not be possible by using more simple equilibrium and kinetic simulations (Ansys Fluent 12.0 Theory Guide, 2009).

On the other hand, the complexity of CFD methods requires from users a good understanding of each field of fluid dynamics (theoretical, experimental and numerical) and knowledge about chemical and physical processes composing on the flow and method of simulating these processes. Users should be aware of simplifications used in the models and application limits connected with them. The mistaken choice of a partial model often leads to the incorrect formulation of the problem and a failure in modeling. The appropriate selection of partial physical models is not a straightforward issue, for example - choosing the best model describing turbulence effect. There are a lot of turbulence models (the more precise are also more computationally expensive), but none of them have universal character, appropriate to every case.

CFD models are also mathematically complicated – for the reason that they are created by partial differential equations which can be solved only in a numerical way in most engineering cases. CFD simulations require a long time for calculations and extremely efficient computers and programs. Furthermore, each numerical method is burdened with discretization error, which may express in the occurrence of artificial source terms with no physical explanation or in diffusion which is more intense than it should be in reality. Discretization errors decrease with the thickening of the grid (but sometimes the solution obtained for a grid with a smaller density is more compatible with experiment results than for models using more dense grids).

Choosing an appropriate length of time step may be a problem in CFD simulations. Too short a time step is linked with lengthy calculations. The determination of too long a time step leads to an increase in approximation error and loss of solution stability (Jaworski, 2005).

4. COMPARATIVE ANALYSIS OF UCG MODELS

Summarizing the considerations presented in part I (equilibrium models) and the current article, it could be general stated, that equilibrium models treat the gasification process overall (both in time in space) while the kinetic and CFD approaches are concern with stages, rates and mechanisms. It is also necessary to indicate that kinetic and CFD models, in some cases, can not be considered as alternatives – source term S_α in equation (18), describing changes in the concentrations of substances, is calculated by using different methods.

The simplest of them is based on Arrhenius equations and kinetic parameters. Therefore, it could be said that (to some extent) the CFD approach is an extension of a kinetic one.

There are also another similarities between the aforementioned three models. Firstly, in each case material balance must be ensured. Secondly, models described in the article are concerned with only one part of the gasifying process – the UCG reactor. When it is necessary to consider the overall technology (for example IGCC), then models presented here are only a point of reference for further simulations.

Nevertheless the differences between equilibrium, kinetic and CFD model are more significant and noticeable.

In order to compare UCG models presented in this article, their most important features were colleted in the table below (Table 4). Comparative analysis is concerned with basic assumptions of the models, their mathematical representation, required inputs, etc.

Table 4. Comparison of UCG models

	Equilibrium model	Kinetic model	CFD model
equilibrium state	+	–	–
state	steady state	transient state	steady or transient state
homogeneity	homogenous	heterogeneous	heterogeneous
knowledge about reactions in system	stoichiometric method – required, non – stoichiometric method – not required	required	required
reactor geometry	–	–	+
changes of parameters in time	–	+	+
mathematical representation	set of non-linear equations	set of ordinary differential equations	set of partial differential equations
numerical methods	Newton method	Runge-Kutta method	finite differences, elements, volumes method
demand for computational power	small	small	large
dedicated software	not required	not required	required
computation time	short	short	long
required input parameters	T, p, gasifying medium composition	T, gasifying medium composition (fractional char conversion)	model requires a lot of inputs: T, p, gasifying medium composition and its parameters (i.a. λ, μ, ρ, c_p), another parameters e.g. channel roughness, turbulence intensity
required constants	equilibrium constants, thermodynamic parameters (specific heat, standard enthalpy and entropy of species), R	kinetic parameters (activation energies, pre-exponential factors, temperature exponents), R, (if reversible reactions are considered also equilibrium constants are required)	thermodynamic parameters, kinetic parameters, constants connected with turbulence, values of characteristic numbers (e.g. Re, Pr)
included phenomena	–	possibility of including diffusion or convection in kinetic equation	turbulence, heat transfer, multi – phase flow
fuel characteristic	some methods include fuel composition	fuel composition, porosity, size of pores	permeability, porosity, λ, c_p, chemical composition
result	equilibrium composition of syngas	changes of syngas composition as function of time	spatial distribution of T, p, species concentrations in reactor
disadvantages/ problems	assumption of equilibrium state	determination of kinetic parameters	computationally expensive, complexity may cause problems

This table clearly shows how the most popular UCG models are different. The presented compilation also indicates how many factors should be taken into account at the stage of choosing an appropriate model for the determined purpose. Above all, the following aspects and problems ought to be considered:

1) Could the reacting system have reached equilibrium state? In some cases thermodynamic models could not be applied,

what is connected with the time of the process being too short or too low temperature in the reactor.

2) Is it required to include changes of parameters in time or in space of the reactor, or both in time and in space? In the second and third case a CFD model will be the best option because it is three dimensional and time dependable. Therefore, it allows for calculations concerning, for example, different configurations of the gasifying channel (and simplifies choosing the best one). The extension of the CFD model also enables us to predict cavity growth (which is a very important aspect of the UCG process). In contrast, the equilibrium model is 0-dimensional and operates in a steady state. Therefore it may correctly simulate stable work of the reactor, but it is not suitable for describing other stages of gasification, like seam ignition or process initialization.

It also should be stated that a CFD model may operate both in steady and transient state (first case takes place when accumulative terms[1] in the transport equation are equal to zero), therefore results from this model may be compared with results from equilibrium (steady state) and kinetic (transient state) simulations.

3) What reactions should be contained in the model? Stoichiometric equilibrium simulations are practically based on the same set of four reactions (when sulfur components are considered this number may increase to eight). Consequently, results from these kind of models can be easily compared. But on the other hand, stoichiometric equilibrium algorithms do not enable the inclusion of other reactions (for example the production of nitrogen compounds, conversion of hydrocarbons). In this situation a choice of kinetic and CFD approaches will be a better option (provided that the required data will be available)[2]. Nevertheless kinetic approach is vulnerable to choice of determined reactions. The exclusion of even one reaction from the system leads to changes in the results obtained.

4) What data is available (and what incompatibility connected with this data is permissible)? Equilibrium models only require information about the composition of the gasifying agent (in some cases also fuel composition), process parameters (temperature and pressure) and equilibrium constants of reactions (this in the case of a stoichiometric approach). Equilibrium constants are relatively simple to obtain – from thermodynamic tables, approximated equations or precise calculations (then more information about specific heat and standard enthalpy and entropy of species is required[3]).

The kinetic approach also requires information about the process parameters (temperature and the converting medium composition). The problem connected with these kinds of models lies in the collection of the kinetic parameters (activation energies, pre-exponential factors, temperature exponents). Obviously this data is easily accessible in literature, but the differences between them, according to analyzed references, may be significant. What is more, when reversible reactions are considered, the model is burdened by mistakes connected with the determination of the equilibrium constant

---

[1] First term in equation, including time.
[2] Non-stoichiometric approach provides information about every required compounds but does not consider stages of process.
[3] Data, which could be easily found in most thermodynamic handbooks.

(because the kinetic constant of a backward reaction is calculated from this parameter).

CFD modeling requires a lot of inputs – process parameters (temperature and pressure), detailed characteristics of the converting agent (not only composition but also viscosity, density, thermal conductivity, etc.), data connected with each species in the reacting system (for example diffusion coefficients), properties of fuel (which will be discussed in the following point), values of many characteristic numbers connected with fluid flow (ex. Reynolds number, Prandtl number), information which leads to calculate source term S_α (in many cases kinetic parameters). When the related physical processes are included in simulations, characteristic features of these phenomena (ex. turbulence intensity) must also be collected.

5) <u>What information about the fuel is obtainable?</u> In equilibrium models only the composition of the fuel is considered. In many cases, when the structure of coal should be taken into account, it is insufficient. Then it is necessary to apply a kinetic (in which the consideration of char structure and porosity are possible) or a CFD approach (which enables the inclusion of many parameters of fuel or the coal seam – porosity, permeability, specific heat, heat transfer coefficient, heat of combustion etc.).

6) <u>Is a very detailed model required, what related phenomena should be included in simulations?</u> Generally, as the level of complexity grows, simulation becomes more difficult and longer, which is connected with the mathematical representation of the model. More complicated mathematical relations describing the reacting system need more advanced numerical methods for finding solutions. Methods dedicated for the solving of partial differential equations, are in their mechanics and algorithms, significantly more complicated (and more difficult to explain) than the Newton method (for solving non-linear equations) or the Runge-Kutta method (ordinary differential equations). This fact has an influence on the requirements connected with the required software and demand for computational power (described in the next point).

The second part of this question is related to the phenomena included in the model. The equilibrium approach does not consider any physical processes, it is only concentrated on gasification. A kinetic approach enables the inclusion in calculations (by modifying kinetic equations) of transport phenomena (ex. diffusion), and what is important, permits the simulation of the pyrolysis process (which is impossible in an equilibrium approach). A CFD model provides information about the large scope of phenomena connected with gasification – devolatilization, turbulence, heat transfer, diffusion, fluid compressibility, so this most completely reflects the behavior of a real reactor. On the other hand CFD codes are very complicated.

It should be highlighted, that the construction of a complex model is not necessary in each case (preliminary optimization, for example). In the opinion of the author equilibrium simulations are better tools for projecting the process (quick determination of the most beneficial choice of gasifying agent composition, temperature, pressure), while the kinetic and CFD approaches give information necessary to reactor design (time of residence, rate of injection of gasifying agent).

7) <u>What is the efficiency of computer and what software is available?</u> CFD models, for example, require specialist and expensive programs like ANSYS FLUENT, COMSOL MUTLIPHYSICS. These simulations are time consuming and need efficient computers. Kinetic and equilibrium models may be easily implemented to commercial mathematical programs (Matlab, MathCAD, Mathematica). Equilibrium algorithms could also be solved by using an Excel Spread Sheet or even an ordinary calculator but it is connected with the iterative procedure (consequently the time taken to find results is longer).

5. CONCLUSIONS

1. Underground coal gasification, as a complex and technically difficult process, often requires the support given by mathematic models. The most commonly used UCG models can be divided into equilibrium, kinetic and CDF approaches.
2. Kinetic and equilibrium models are computationally simpler and faster convergent than CFD ones. They also do not require dedicated software – simulations could be carried out with commercial computation programs, like Mathematica.
3. Residence time and temperature of gasification are basic criteria which determine the choice of either a kinetic or equilibrium model. For processes proceeding with a fast rate or in a short time only kinetic models may be used (because the system is not in a state of equilibrium in these conditions).
4. CFD models have many advantages which do not apply to kinetic and equilibrium simulations – i.e. they include complex phenomena which occur in gasification or permit 3-D simulations. On the other hand, these kinds of models require much input data, large amounts of computational power, a long time for calculations and, above all, a high level of the user's knowledge.
5. The determination of equilibrium and kinetic constant values is one of the most common difficulties which occurs in model formulation. These values may significantly differ according to the quoted source. Moreover, previously mentioned constants were obtained in experiments, whose conditions may vary from real the conditions of the process.
6. A universal model of UCG had not been constructed to date. Therefore, choice of simulation method should depend on determined aims. For example, an equilibrium model is sufficient for the preliminary analysis of the process, hence complicated and time-consuming CFD simulations are not necessary in this case.

References
Ahmed, T., Ahmad, M., Yusup, S., Inayat, A., & Khan, Z. (2012). Mathematical and computational approaches for design of biomass gasification for hydrogen production: A review. *Renewa-*

ble and Sustainable Energy Reviews, *16*(4), 2304–2315. doi: 10.1016/j.rser.2012.01.035.

Ansys Fluent 12.0 Theory Guide. (2009). ANSYS, Inc.

Atkins, P. (2001). *Chemia fizyczna* [Physical chemistry]. Warszawa: PWN.

Bhutto, A., Bazmi, A., & Zahedi, G. (2013). Underground coal gasification: From fundamentals to applications. *Progress in Energy and Combustion Science*, *39*(1), 189–214. doi: 10.1016/j.pecs. 2012.09.004.

Białecka, B. (2008). *Podziemne zgazowanie węgla – podstawy procesu decyzyjnego* [Underground coal gasification – basics of the decision-making process]. Katowice: Główny Instytut Górnictwa.

Boiko, E.A., & Pachkovskii, S.V.A. (2004). Kinetic Model of Thermochemical Transformation of Solid Organic Fuels. *Russian Journal of Applied Chemistry*, *77*(9), 1547–1555. doi: 10.1007/s11167-005-0070-0.

Chaiyot, T., Supunnee, J., & Juejun, K. (2013). Comparison of Kinetic Models for CO_2 Gasification of Coconut-Shell Chars: Carbonization Temperature Effects on Char Reactivity and Porous Properties of Produced Activated Carbons. *Engineering Journal*, *17*(1), 13–27. doi: 10.4186/ej.2013.17.1.

Chen, C.J., Hung, C.I., & Chen, W.H. (2012). Numerical investigation on performance of coal gasification under various injection patterns in an entrained flow gasifier. *Applied Energy*, *100*, 218–228. doi: 10.1016/j.apenergy.2012.05.013.

de Souza-Santos, M.L. (2004). *Solid Fuels Combustion and Gasification: Modeling, Simuation and Equipment Operation.* New York: Marcel Dekker Inc.

Golec, T., Ilmurzyńska, J. (2008). Modelowanie procesów zgazowania [Modeling of gasification process]. In T. Borowiecki, J. Kijeński, J. Machnikowski, & M. Ściążko (Eds.), *Czysta energia, produkty chemiczne i paliwa z węgla – ocena potencjału rozwojowego* (pp. 170–187). Zabrze: Wydawnictwo Instytutu Chemicznej Przeróbki Węgla.

Gómez-Barea, A., & Leckner, B. (2010). Modeling of biomass gasification in fluidized bed. *Progress in Energy and Combustion Science*, *36*(4), 444–509. doi: 10.1016/j.pecs.2009.12.002.

Jaworski, Z. (2005). *Numeryczna mechanika płynów w inżynierii chemicznej i procesowej* [Computational fluid dynamics in chemical and process engineering]. Warszawa: Akademicka Oficyna Wydawnicza EXIT.

Li, Z.Q., Wei, F., & Jin, Y. (2003). Numerical simulation of pulverized coal combustion and NO formation. *Chemical Engineering Science*, *58*(23-24), 5161–5171. doi: 10.1016/j.ces.2003.08.012.

Łabojko, G., Morańska-Kotyczka, M., Plis, A., & Ściążko, M. (2012). Kinetic study of Polish hard coal and its char gasification using carbon dioxide. *Thermochimica Acta*, *549*(10), 158–165. doi: 10.1016/j.tca.2012.09.029.

Pèrez-Fortes, M., & Bojarski, A. (2011). Modelling Syngas Generation. In L. Puigjaner (Ed.), *Syngas from Waste: Emerging Technologies* [pp. 55–88]. London: Springer-Verlag London Limited.

Puig-Arnavat, M., Bruno J.C., & Coronas, A. (2010): Review and analysis of biomass gasification models. *Renewable and Sustainable Energy Reviews*, *14*(9), 2841–2851. doi: 10.1016/j.rser.2010.07.030.

Silaen, A., & Wang, T. (2009). Comparison of instantaneous, equilibrium, and finite-rate gasification models in an entrained-flow coal gasifier. In *Proceedings of the 26th International Pittsburgh Coal Conference* (pp. 1–11). Pittsburgh, PA: University of Pittsburgh.

Silaen, A., & Wang, T. (2010). Effect of turbulence and devolatization models on coal gasification simulation in entrained-flow gasifier. *International Journal of Heat and Mass Transfer*, *53*(9-10), 2074-2091. doi: 10.1016/j.ijheatmasstransfer.2009.12.047.

Tabiś, B. (2002). *Zasady inżynierii reaktorów chemicznych* [Principles of chemical reactors engineering]. Warszawa: WNT.

Tomeczek, J. (1992). *Spalanie węgla* [Coal combustion]. Gliwice: Wydaw. Politechniki Śląskiej.

Wachowicz, J., Janoszek, T., & Iwaszenko, S. (2010). Model tests of the coal gasification process. *Archives of Mining Sciences*, *55*(2), 245–258.

Watanabe, H., & Otaka, M. (2006). Numerical simulation of coal gasification in entrained flow coal gasifier. *Fuel*, *85*(12-13), 935–943. doi: 10.1016/j.fuel.2006.02.002.

Williams, A., Pourkashanian, M., & Jones, J.M. (2001). Combustion of pulverized coal and biomass. *Progress in Energy and Combustion Science*, *27*(6), 587–610. doi: 10.1016/S0360-1285(01)00004-1.