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Numerical study with ChemKin for hydrogasification mechanism of pulverized coal and Hg speciation transformation inside a hydrogasifier

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Zero-emission coal (ZEC) technology has been actively studied recently. It aims to achieve zero emission of CO_2 and other pollutants and the efficiency of this system can reach no less than 70%. Hydro-gasification of pulverized coal is a core process of ZEC. However, the mechanism of gasification and transformation of mercury speciation in the hydro-gasification is has not been understood precisely up until now. This restrains the ZEC's commercialization. The purpose of this paper is to study the mechanism of hydro-gasification and mercury speciation transformation for coal in the gasifier with high temperature and pressure. Detailed chemical kinetics mechanism (CKM) has been proposed for hydro-gasification for pulverized coal in an entrained flow hydro-gasifier. The effects have been studied for different reaction conditions on hydro-gasification products and evolution of Hg in terms of the chemical reaction kinetics method. The CKM mechanism includes 130 elementary reactions and is solved with commercially available software, ChemKin. The calculation results are validated against the experimental data from literature and meaningful predictions are finally obtained. In addition, the chemical equilibrium calculation (CEC) is also used for predictions. Although the CEC method assumes all the reactions have reached chemical equilibrium, which is not the case in industrial reality, the calculation results are of value as reference.

Numerička studija izrađena pomoću ChemKin za rasplinjavanje vodene pare ugljene prašine i transformacije žive unutar rasplinjača s vodenom parom*

Izvorni znanstveni rad

Tehnologija korištenja ugljena bez emisija (ZEC) se od nedavno aktivno proučava. Njezin cilj je postizanje nulte stope emisija CO_2 te ostalih štetnih tvari dok efikasnost sustava mora biti minimalno 70%. Rasplinjavanje ugljene prašine vodenom parom je temeljni proces ZEC-a. Međutim, mehanizam rasplinjavanja i transformacije žive u rasplinjavanju vodenom parom još nije u potpunosti shvaćeno. To ograničava mogućnost komercijalne primjene ZEC-a. Cilj ovog rada je proučavanje mehanizama rasplinjavanja vodenom parom i transformacije žive za rasplinjavanje ugljena u rasplinjaču s visokim temperaturama i tlakom. Predloženi su detaljni kemijski kinetički mehanizmi (CKM) za rasplinjavanje ugljene prašine u fluidiziranom sloju sa zajedničkim tokom tvari. Proučeni su utjecaji raznih uvjeta pod kojim su se odvijale reakcije na produkte rasplinjavanja i evoluciju žive u uvjetima kemijskih reakcija kinetičke metode. CMK mehanizam sadrži 130 elementarnih reakcija i rješava se s komercijalno dostupnim programom, ChemKin. Rezultati simulacije se uspoređuju s eksperimentalnim iz literature te su konačno dobivena smislena predviđanja. Jednadžbe kemijske ravnoteže (CEC) su također korištene za predviđanja. Iako CEC metoda pretpostavlja da su sve reakcije postigle ravnotežu, što nije uvijek slučaj u industriji, rezultati tog proračuna mogu poslužiti kao referenca.

1. Introduction

With the increasing utilization of fossil fuel, environmental damage is becoming more and more severe worldwide [1, 2]. Although many new clean alternative energy sources have been developed, coal is still expected to be the major fuel in the future for its abundance and wide geographic distribution. Other alternative energy sources are not sufficient enough to cover the great energy increase of the world [3, 4]. The process of the zero-emission coal (ZEC) concept was first proposed by researchers at the Los Alamos National Laboratory (LANL) and Louisiana State University, U.S.A. It is generally referred as the LANL ZEC technology [5-9]. Recently, increasing attention has been paid to ZEC technology because the amount of CO_2 and other pollutants emissions can be nearly zero and the total efficiency can reach no less than 70%. Based on the LANL ZEC technology, coal, as shown in Fig.1, is hydro-gasified to generate a gas stream of rich methane, called syngas, in a gasification vessel. This syngas passes a high-temperature cleanup train to remove particles and most sulphides. The cleaned syngas enters the reformers (the carbonation vessels) where the methane is reformed with steam in the presence of CaO to produce a hydrogen rich stream. The hydrogen produced by carbonation vessel A is recycled to the gasification vessel for the next hydro-gasification of coal, and the hydrogen produced by carbonation vessel B is sent to a solid oxide fuel cell (SOFC) for electricity generation. The inevitable waste heat generated in the SOFC is transferred by the CO_2 stream to the calcination vessels to decompose $CaCO_3$ produced in the carbonation vessels, and a pure stream of CO_2 is produced for sequestration or other utilizations. The steam produced in the SOFC is fed into the carbonation vessels for methane production [10-12]. The hydro-gasifier for pulverized coal, as shown in the dashed box in Fig.1, is the core equipment of the ZEC system. The gasification mechanism and the progress of mercury (Hg) speciation transformation in the gasifier, however, are not understood thoroughly. If this novel system is to be commercially developed, the reaction mechanism including the transformation mechanism of the heavy metal, such as Hg, in the reactor must be known clearly.

Symbols/Oznake

a,b,c,d,e,f	- stoichiometric factors/ Stehiometrijski faktori	R	- universal gas constant/ univerzalna plinska konstanta, 8.3145 J/(mol·K)
C_{pi}	- specific heat/ specifična toplina, J/(mol·K)	T_R	- reaction temperature/ temperature koncentracije, K
E_a	- activation energy/ aktivacijska energija, cal/mol	x_i, w, m	- amount of substance of species *i/ količina tvari kemijske vrste i*, mol
f_i	- mole concentration of species *i/ molarna koncentracija kemijske vrste i*		**Greek letters/Grčka slova**
ΔG^0	- standard Gibbs energy of formation/ standardna Gibbsova energija formacije, J/mol	β	- temperature exponent/ eksponent temperature
H_i	- heat of formation of species *i/ toplina formacije kemijske vrste i*, J/mol		**Subscripts/Indeksi**
K_0	- pre-exponential factor/ pred eksponencijalni faktor, (cm, K, s, mol)	n	- mole ratio of H to C in coal/ omjer molarnog udjela H i C u ugljenu
K_{ci}	- equilibrium constant of reaction *i* denoted by concentration/ konstanta ravnoteže reakcije i obilježena koncentracijom	p	- mole ratio of O to C in coal/ omjer molarnog udjela O i C u ugljenu
K_{pi}	- equilibrium constant of reaction *i* denoted by partial pressure/ konstanta ravnoteže reakcije i obilježena parcijalnim tlakom	q	- mole ratio of N to C in coal/ omjer molarnog udjela N i C u ugljenu
P_R	- reaction pressure/ tlak reakcije, Pa	r	- mole ratio of S to C in coal/ omjer molarnog udjela S i C u ugljenu

Therefore, it is urgently important to study the detailed chemical kinetics mechanism of the reaction process.

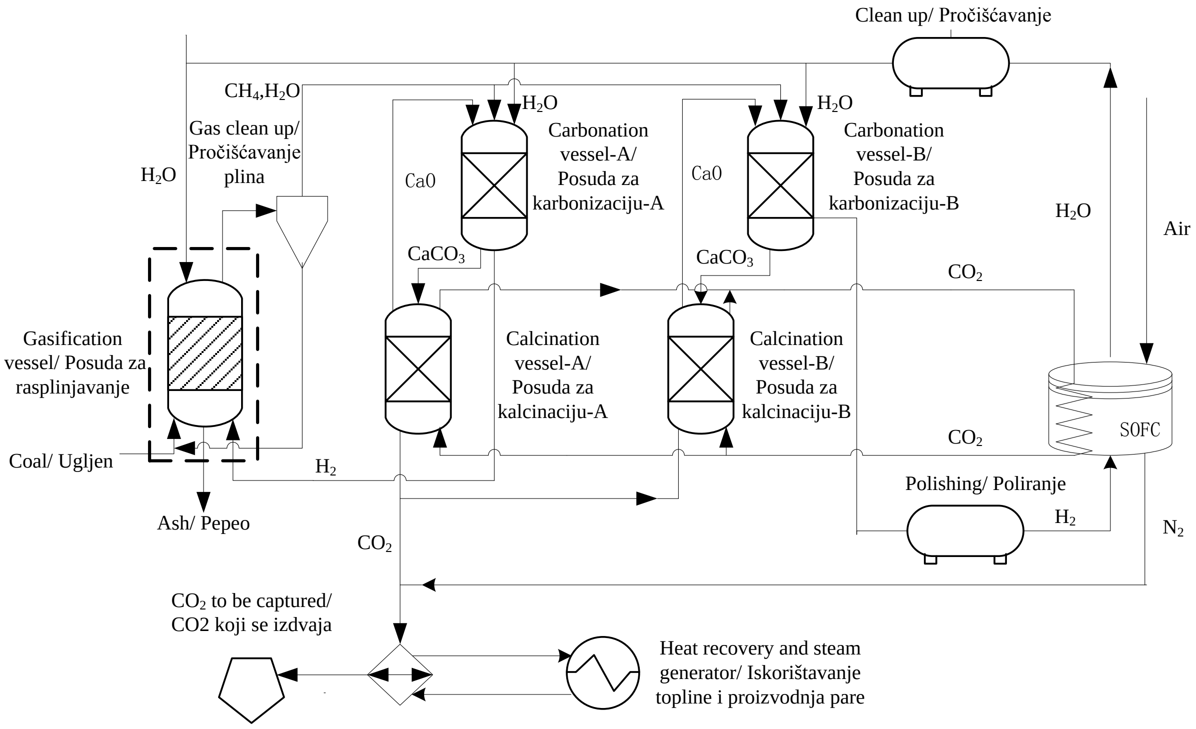


Figure 1. Schematic diagram of the zero-emission coal (ZEC) system
Slika 1. Shema sustava korištenja ugljena bez emisija (ZEC)

2. Chemical Equilibrium and Calculation

2.1. Theory

The chemical equilibrium model assumes that all the reactions proceed in both directions at the same rate. This assumption is sound when the residence time of reactants is long enough in the reactor. But the time needed for some reactions to reach chemical equilibrium is always very long especially when the reaction rate is relatively slow or even immeasurably slow. So in an actual industrial production process, the reactions are always far from chemical equilibrium for the sake of productive efficiency. Some researchers have already done research on biomass and coal gasification using the CEC model [13-16]. Three main equations are taken into account in this calculation including the material balance equation, the chemical equilibrium equation and the energy conservation equation. In the biomass air-gasification process, the molecular formula of biomass is assumed as CH_nO_p and the gasification equation can be expressed as Eq. (1).

$$\begin{aligned}&\mathrm{CH_nO_p} + w\mathrm{H_2O} + m\mathrm{O_2} + 3.76m\mathrm{N_2}\\ &= x_1\mathrm{H_2} + x_2\mathrm{H_2O} + x_3\mathrm{CH_4} + \\ &x_4\mathrm{CO} + x_5\mathrm{CO_2} + 3.76m\mathrm{N_2}\end{aligned} \tag{1}$$

The subscripts, n and p, are based on the ultimate analysis of biomass. The coefficients, w, m, x_1, x_2, x_3, x_4 and x_5 in Eq.(1) are the stoichiometric factors. First, the mass balance is written to indicate the conservation of elements occurring in the gasification process. In this case, there are 4 elements C, H, O and N, and therefore, four material balance equations can be obtained. Then, other reactions also take place in the process, e.g. the methane formation reaction, Eq. (2), and the shift reaction, Eq. (3).

$$\mathrm{C+2H_2 = CH_4} \tag{2}$$

$$\mathrm{CO+H_2O = CO_2 + H_2} \tag{3}$$

For each reaction, such as Eq. (2) or Eq. (3), an equation, like Eq. (4), can be obtained to calculate its equilibrium constant, K_{ci}.

$$K_{ci} = \frac{f_{P1}^{c} f_{P2}^{d}}{f_{R1}^{a} f_{R2}^{b}} \tag{4}$$

where, f_{Pi} is the mole concentration of product *i*; f_{Ri} is the mole concentration of reactant *i*; and *a*, *b*, *c* and *d* are the stoichiometric factors. In addition, the equilibrium constant expressed by the species partial pressure, K_{pi}, can also be written as Eq. (5).

$$-RT\ln K_{pi} = \Delta G^0 \tag{5}$$

where, ΔG^0 is the standard Gibbs energy of formation and K_{ci} and K_{pi} are related by Eq.(6).

$$K_{ci} = K_{pi}(RT)^{-(c+d-a-b)} \tag{6}$$

The heat energy balance of the gasification process is expressed by Eq. (7).

$$\begin{aligned} &H^0_{coal} + wH^0_{\mathrm{H_2O}} + mH^0_{\mathrm{O_2}} + 3.76mH^0_{\mathrm{N_2}} = x_1H^0_{\mathrm{H_2}} \\ &+ x_2H^0_{\mathrm{H_2O}} + x_3H^0_{\mathrm{CH_4}} + x_4H^0_{\mathrm{CO}} + x_5H^0_{\mathrm{CO_2}} + \\ &3.76mH^0_{\mathrm{N_2}} + \Delta T(x_1C_{pH_2} + x_2C_{pH_2O} + \\ &x_3C_{pCH_4} + x_4C_{pCO} + x_5C_{pCO_2} + 3.76mC_{pN_2}) \end{aligned} \tag{7}$$

where, H^0_{i} is the heat of formation of species *i*; C_{pi} is the specific heat of the gaseous products; $\Delta T = T_2 - T_1$ is the temperature difference with T_2 as the gasification temperature at the reduction zone and T_1 as the ambient temperature at the reaction zone. Eqs. (1)-(7) form the thermodynamic model for the process of biomass air-gasification.

In the coal hydro-gasification process, the molecular formula of coal is assumed as $\mathrm{CH_nO_pN_qS_r}$ and the gasification equation can be written as Eq. (8).

$$\begin{aligned} &\mathrm{CH_nO_pN_qS_r} + w\mathrm{H_2O} + y\mathrm{H_2} = x_1\mathrm{H_2} + \\ &x_2\mathrm{H_2O} + x_3\mathrm{CH_4} + x_4\mathrm{CO} + x_5\mathrm{CO_2} \\ &+ x_6\mathrm{COS} + x_7\mathrm{H_2S} + x_8\mathrm{N_2} + x_9\mathrm{C} \end{aligned} \tag{8}$$

The subscripts, n, p, q and r, are based on the ultimate analysis of coal. First, the mass balance is written to reflect the conservation of elements appearing in the gasification process. In this case, there are 5 elements C, H, O, N and S, and therefore, five equations can be obtained. Then, other reactions also take place in this process, e.g. the methane formation reaction shown in Eq. (2), and the shift reaction shown in Eq. (3). Two more reactions, Eqs. (9) and (10), are selected to close the equations (2-6, 8 and 11).

$$\mathrm{CO} + 3\mathrm{H_2} = \mathrm{CH_4} + \mathrm{H_2O} \tag{9}$$

$$\mathrm{COS} + \mathrm{H_2O} = \mathrm{CO_2} + \mathrm{H_2S} \tag{10}$$

For each reaction, such as Eq. (2), Eq. (3), Eq. (9) or Eq. (10) an equation, like Eq. (4), can be written to calculate the equilibrium constant K_{ci} . Again, the equilibrium constant expressed by the species partial pressure, K_{pi} , can be calculated with Eq. (5) and K_{ci} and K_{pi} are related by Eq. (6). The heat energy balance of the gasification process is expressed in Eq. (11).

$$\begin{aligned} &H^0_{coal} + wH^0_{\mathrm{H_2O}} + yH^0_{\mathrm{H_2}} = x_1H^0_{\mathrm{H_2}} + x_2H^0_{\mathrm{H_2O}} + x_3H^0_{\mathrm{CH_4}} \\ &+ x_4H^0_{\mathrm{CO}} + x_5H^0_{\mathrm{CO_2}} + x_6H^0_{\mathrm{COS}} + x_7H^0_{\mathrm{H_2S}} + x_8H^0_{\mathrm{N_2}} + \\ &x_9H^0_{\mathrm{C}} + \Delta T(x_1C_{pH_2} + x_2C_{pH_2O} + x_3C_{pCH_4} + x_4C_{pCO} \\ &+ x_5C_{pCO_2} + x_6C_{pCOS} + x_7C_{pH_2S} + x_8C_{pN_2} + x_9C_{pC}) \end{aligned} \tag{11}$$

Eqs. (2)-(6) incorporated with Eqs. (8)-(11) form the thermodynamic model of the coal hydro-gasification. The equilibrium block of ChemKin in this work is used to solve equations for coal gasification.

2.2. Comparison with published data

The three sets of published data for coal gasification in an entrained flow gasifier [17, 18] are selected for the CEC model validation. Data used for the simulation is listed in Table 1. The detailed boundary conditions can be found in literature [18]. The comparison of simulated results of the equilibrium block and the published data is shown in Table 2. Exp. denotes the experiment results and Cal. denotes the calculated results by CEC model. The model results are found to be in good agreement with the published data because the absolute error of this work is relatively small and this model can be used for further prediction.

Table 1. Data used for the CEC model simulation

Tablica 1. Podaci korišteni u CEC simulaciji

Exp./Eksperiment	Gasification agent to coal mass ratio/Omjer mase medija za rasplinjavanje i ugljena			Pressure/Tlak/ MPa	Ultimate analysis of coal/Konačna analiza ugljena (d)/%					
	$m(O_2)/m(coal)$	$m(H_2O)/m(coal)$	$m(N_2)/m(coal)$		C	H	O	N	S	Ash
I	0.8	0.08	0.130	2.413	69.6	5.3	10.0	1.3	3.9	10.0
II	0.86	0.50	0.017	4.083	69.6	5.3	10.0	1.3	3.9	10.0
III	1.03	0.65	0.000	4.083	86.0	2.0	2.3	1.0	8.3	0.5

Table 2. Comparison between the CEC model results and the experiments data

Tablica 2. Usporedba rezultata dobivenih CEC modelom i eksperimentalnih podataka

Species/ Vrsta	Exp. 1/Eksperiment 1/ [17, 18]	Cal. 1/ Proračun 1	Exp. 2/ Eksperiment 2 [17, 18]	Cal. 2/ Proračun 2	Exp. 3/ Eksperiment 3 [17, 18]	Cal. 3/ Proračun 3
CO	61.5	59.4	41.0	40.1	47.10	47.8
CO_2	1.6	1.47	10.2	10.7	13.20	12.4
H_2	30.6	29.4	29.8	30.02	24.30	23.3
H_2O	—	2.17	17.1	16.4	12.70	13.6
CH_4	0	0	0.3	0.27	0.09	0.09

N_2	4.7	5.43	0.8	0.95	0.40	0.30
H_2S	1.2	1.20	1.1	1.03	2.20	2.06

2.3. Predictions of coal hydro-gasification using the equilibrium block

After being validated, the CEC model can be then used to model the coal hydro-gasification process proceeded in the ZEC hydro-gasifier. Initial species mole fractions are listed in Table 3 with a value of *U*, the H_2/coal mass ratio, of 0.4. The reaction temperature T_R, pressure p_R and the H_2/coal mass ratio *U* are the most important operation parameters for the hydro-gasification process and have significant effects on the gasification products. They are then selected for the sensitivity analysis in this work. The effects of these parameters on the coal hydro-gasification products and mercury transformation process are shown in Figs. 2-7 when all the reactions approach thermodynamic equilibrium.

Table 3. Initial species mole fraction of the reactant mixture with H2/coal mass ratio of 0.4

Tablica 3. Inicijalne vrste molarne frakcije mješavine reaktanta sa masenim omjerom H2/ugljen of 0.4

Species/ Kemijska vrsta	Hg	Cl	C(s)	C	H	O	N	S	H_2	H_2O
Mole fraction/ Molna frakcija	3.17E-9	4.47E-5	1.50E-1	5.01E-2	1.38E-1	2.47E-2	1.49E-3	7.63E-4	6.35E-1	3.53E-4

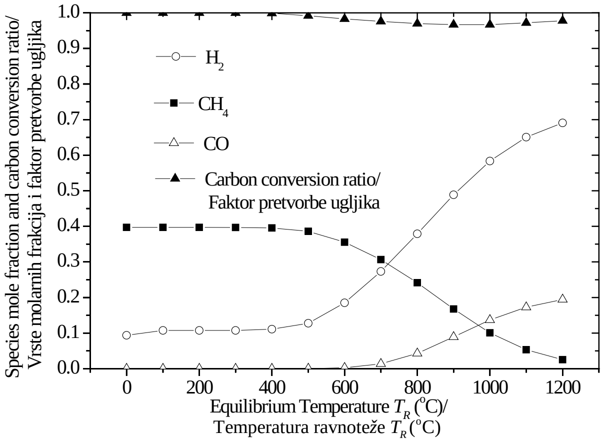


Figure 2. Effects of T_R on mole fraction of gasification products and carbon conversion ratio with *U* of 0.4 and p_R of 70 atm

Slika 2. Utjecaj T_R na molarne udjele produkata rasplinjavanja i faktor pretvorbe ugljika uz U=0.4 i p_R=70 atm

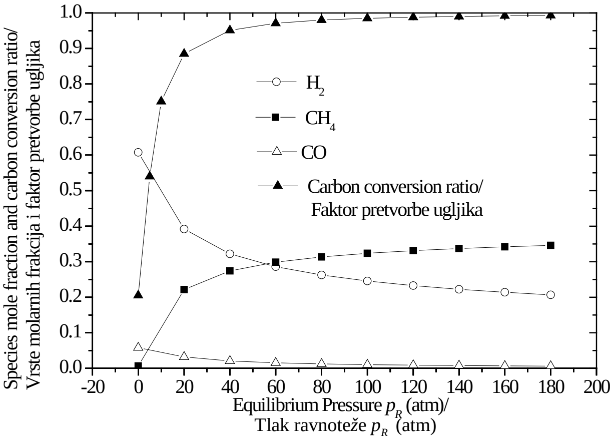
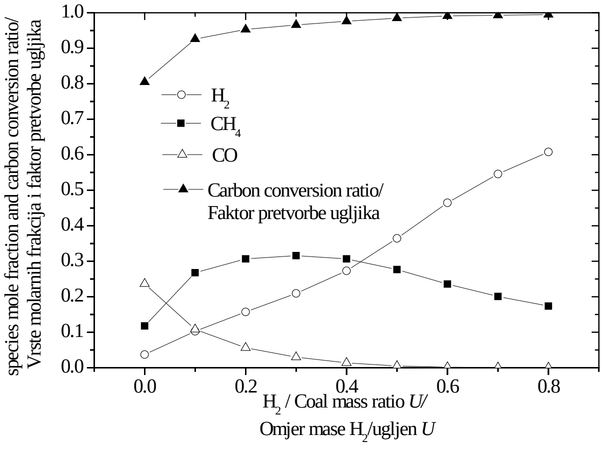


Figure 3. Effects of p_R on mole fraction of gasification products and carbon conversion ratio with *U* of 0.4 and T_R of 700°C

Slika 3. Utjecaj p_R na molarne udjele produkata rasplinjavanja i faktor pretvorbe ugljika uz U=0.4 i T_R=700°C



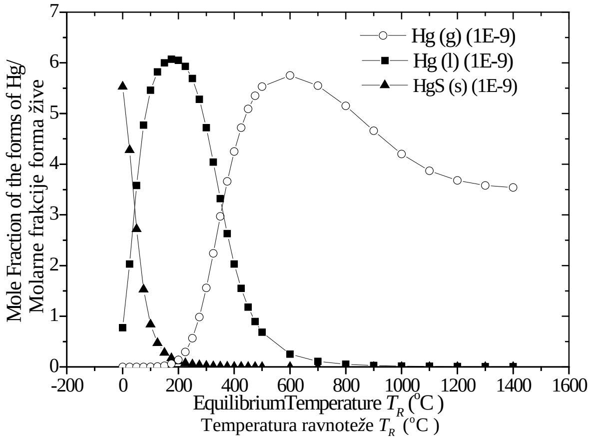


Figure 4. Effects of *U* on mole fraction of gasification products and carbon conversion ratio with T_R of 700°C and p_R of 70 atm

Slika 4. Utjecaj U na molarne udjele produkata rasplinjavanja i faktor pretvorbe ugljika uz T_R =700°C i p_R=70 atm

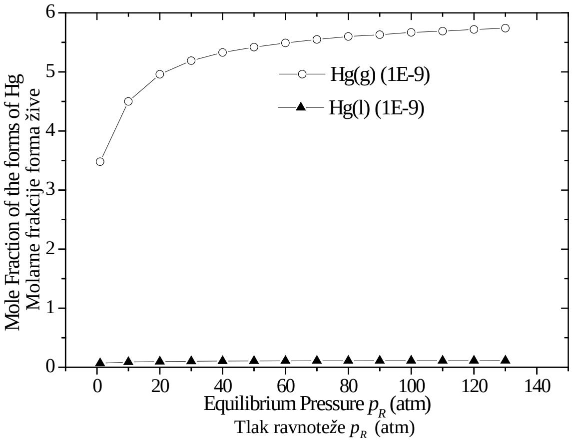


Figure 6. Effects of p_R on mercury specific transformation with *U* of 0.4 and T_R of 700°C

Slika 6. Utjecaj p_R na transformaciju žive uz U=0.4 i T_R=700°C

The influences of the reaction temperature T_R on the gasification products and the carbon conversion ratio are shown in Fig. 2. The carbon conversion ratio and the CH_4 mole fraction decrease as T_R increases while the H_2 mole fraction increases with the increase of T_R. This is consistent with the fact that the methane formation reaction is an exothermic process. The CO mole fraction increases with the increase of T_R because the CO formation reaction is an endothermic process. The influences of the reaction pressure p_R on gasification products and the carbon conversion ratio are shown in Fig. 3. The mole fractions of species are very sensitive to the changes of p_R when the reaction pressure is lower than 60 atm. The CH_4 mole fraction and the carbon conversion ratio increase sharply with the increase of p_R and H_2 and the CO mole fractions decrease quickly as the p_R increases. Since the CH_4 formation reaction decreases, the amount of substance in the gasifier, the dissociation degree of CH_4 will decrease with the increase of p_R. The reaction of methane formation, Eq. (2), will then move forward. When p_R is higher than 60 atm, mild effects will be generated on the gasification products. The effects of the H_2/coal mass ratio *U* on gasification products and the carbon conversion ratio are shown in Fig. 4. The mole fraction of H_2 increases with the increase of *U*, while the CO mole fraction decreases as *U* increases. The CH_4 mole fraction increases as *U* increases when the H_2/coal mass ratio is less than about 0.3, and decreases when *U* is greater than 0.3. This is because the complete reaction of 12 g (1mol) C to form CH_4 needs 4 g (2 mol) H_2. For this case, the mass ratio of H_2/coal is 0.333. If *U* is larger than this value, there will not be enough C to sustain the reaction. On the contrary, the excessive H_2 will dilute the products.

Figure 5. Effects of T_R on mercury specific transformation with *U* of 0.4 and p_R of 70 atm

Slika 5. Utjecaj T_R na transformaciju žive uz U=0.4 i p_R=70 atm

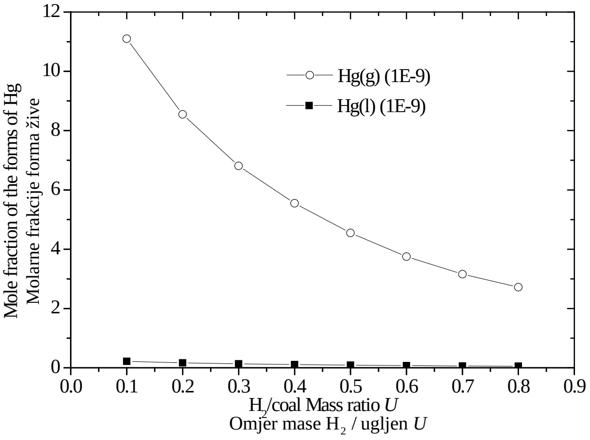


Figure 7. Effects of *U* on mercury specific transformation with T_R of 700°C and p_R of 70 atm

Slika 7. Utjecaj U na transformaciju žive uz T_R =700°C i p_R=70 atm

The influences of T_R on mercury transformation are shown in Fig. 5. With the increase of T_R, liquid mercury Hg (l) and solid mercuric sulphide, HgS(s), are gradually transformed to mercury vapour, Hg (g). When T_R is greater than 400°C, mercuric sulphide will be completely transformed to elemental mercury. The higher the equilibrium temperature, the more gaseous the mercury in the mixture of products appears. The influences of p_R on mercury transformation are shown in Fig. 6. Both the mole fractions of the liquid and gaseous mercury increase slightly with the increase of p_R. The influences of *U* on mercury transformation are shown in Fig. 7. Both the liquid and gaseous mercury mole fractions slightly decrease as *U* increases, due to the dilution effect of excessive H_2.

If all reactions reach their chemical equilibrium, mercury as in the oxidised form is mainly HgS (s) with a small amount of HgCl or $HgCl_2$.

3. Chemical Kinetics

3.1. Theory

For a complex chemical reaction process, a group of reaction rate equations based on this mechanism can be set up with the known chemical reaction kinetic mechanism. Assuming that there are m species and n elementary reactions, the group of reaction rate equations will then consist of m equations and can be written in matrix form as in Eq. (12).

$$\begin{bmatrix} dc_1/dt \\ dc_2/dt \\ \vdots \\ dc_m/dt \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22} & \cdots & a_{2n} \\ & \cdots & \cdots & \\ a_{m1} & a_{m2} & & a_{mn} \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \\ \vdots \\ v_n \end{bmatrix} \tag{12}$$

where, $\mathrm{d}c_\mathrm{i}/\mathrm{d}t$ is the formation or consumption rate of species i; a_ij is the stoichiometric number of species i in the elementary reaction j; v_j is the reaction rate of the elementary reaction j, e.g., $a\mathrm{A}+b\mathrm{B}+c\mathrm{C}+\cdots=d\mathrm{D}+e\mathrm{E}+f\mathrm{F}+\cdots$, and can be calculated using the mass action law, Eq. (13).

$$v_i = kC_A^a C_B^b C_C^c \dots \tag{13}$$

where, C_A, C_B, C_C and so on are the concentrations of the reactants in the reaction system; a, b, c and so on are the stoichiometric factors of reactants in the elementary reactions; k is the rate constant and can be calculated using the corrected Arrhenius equation, Eq. (14).

$$k = k_0\left(\frac{T}{T_0}\right)^{\beta} e^{-E_a/RT} \tag{14}$$

where, k_0, n and E_a are the pre-exponential factor, the temperature exponent and the activation energy, respectively, and can be determined by experiments as shown in Tables 4-9 [19-28].

The specific equation group to calculate the coal hydro-gasification reaction rate will not be set up in this paper. ChemKin is, instead, chosen to do the calculation. But, a detailed reaction kinetic mechanism to properly reflect the complex reaction process needs to be set up [29]. A homogeneous reaction kinetic mechanism for coal hydro-gasification is set up in this paper. There are 21 elementary reactions for H, 8 for Hg, 16 for Cl, 66 for C, 7 for S and 12 for N, respectively. The 130 elementary reactions used in total are listed in Tables 4-9 [19-28].

Table 4. Twenty one (21) elementary reactions for H [19]

Tablica 4. Dvadeset i jedna (21) elementarna reakcija vodika H [19]

	Pre-exponential factor/Faktor k_0 (cm, K, s, mol)	Temperature index/ Temperaturni indeks β	Activation energy/ Aktivacijska energija E_a (cal/mol)
$H+O_2$ <=> O+OH	1.915E+14	0.00	1.644E+04
$O+H_2$ <=> H+OH	5.080E+04	2.67	6.292E+03
$OH+H_2$ <=> $H+H_2O$	2.160E+08	1.51	3.430E+03
$O+H_2O$ <=> OH+OH	2.970E+06	2.02	1.340E+04
H_2+M <=>H+H+M	4.577E+19	1.40	1.044E+05
O_2+M <=> O+O+M	4.515E+17	0.64	1.189E+05
OH+M <=> O+H+M	9.880E+17	0.74	1.021E+05
H_2O+M <=> H+OH+M	1.912E+23	-1.83	1.185E+05
$H+O_2(+M)$ <=> $HO_2(+M)$	1.475E+12	0.60	0.000E+00
HO_2+H <=> H_2+O_2	1.660E+13	0.00	8.230E+02
HO_2+H <=> OH+OH	7.079E+13	0.00	2.950E+02
HO_2+O <=> $OH+O_2$	3.250E+13	0.00	0.000E+00
HO_2+OH <=> H_2O+O_2	2.890E+13	0.00	4.970E+02
$H_2O_2+O_2$<=> HO_2+HO_2	4.634E+16	0.35	5.067E+04
$H_2O_2+O_2$ <=> HO_2+HO_2	1.434E+13	0.35	3.706E+04
$H_2O_2(+M)$ <=> OH+OH(+M)	2.951E+14	0.00	4.843E+04
H_2O_2+H <=> H_2O+OH	2.410E+13	0.00	3.970E+03
H_2O_2+H <=> H_2+HO_2	6.025E+13	0.00	7.950E+03
H_2O_2+O <=> $OH+HO_2$	9.550E+06	2.00	3.970E+03
H_2O_2+OH <=> H_2O+HO_2	1.000E+12	0.00	0.000E+00
H_2O_2+OH <=> H_2O+HO_2	5.800E+14	0.00	9.557E+03

Table 5. Eight (8) elementary reactions for Hg [20]

Tablica 5. Osam (8) elementarnih reakcija žive Hg [20]

	Pre-exponential factor/Faktor k_0 (cm, K, s, mol)	Temperature index/ Temperaturni indeks β	Activation energy/ Aktivacijska energija E_a (cal/mol)
Hg+Cl+M<=>HgCl+M	9.00E+15	0.5	0
Hg+Cl2<=>HgCl+Cl	1.39E+14	0	34000
Hg+HCl<=>HgCl+H	4.94E+14	0	79300
Hg+HOCl<=>HgCl+OH	4.27E+13	0	19000
$HgCl+Cl_2$<=>$HgCl_2+Cl$	1.39E+14	0	1000
HgCl+Cl+M<=>$HgCl_2+M$	1.16E+15	0.5	0
HgCl+HCl<=>$HgCl_2+H$	4.64E+03	2.5	19100
HgCl+HOCl<=>$HgCl_2+OH$	4.27E+13	0	1000

Table 6. Sixteen (16) elementary reactions for Cl [21]

Tablica 6. Šesnaest (16) elementarnih reakcija klora Cl [21]

	Pre-exponential factor/Faktor k_0 (cm, K, s, mol)	Temperature index/ Temperaturni indeks β	Activation energy/ Aktivacijska energija E_a (cal/mol)
Cl+Cl<=>Cl_2	3.70E-10	0	-1800
HCl+H<=>H_2+Cl	1.44E+13	0	3400
H+Cl_2<=>HCl+Cl	8.61E+13	0	1170
O+HCl<=>OH+Cl	6.02E+05	2.11	4020
OH+HCl<=>Cl+H_2O	1.11E+07	1.66	-660
O+Cl_2<=>ClO+Cl	2.51E+12	0	2720
O+ClO<=>Cl+O_2	5.70E+13	0	360
Cl+HO_2<=>HCl+O_2	1.08E+13	0	-340
Cl+HO_2<=>OH+ClO	2.47E+13	0	890
Cl+H_2O_2<=>HCl+HO_2	6.62E+12	0	1950
ClO+H_2<=>HOCl+H	6.62E+03	0	0
H+HOCl<=>HCl+OH	3.18E+09	1.2	370
Cl+HOCl<=>HCl+ClO	3.55E-01	4.07	-340
Cl_2+OH<=>Cl+HOCl	1.61E+06	2.1	1150
O+HOCl<=>OH+ClO	1.02E+11	0	0
OH+HOCl<=>H_2O+ClO	1.81E+12	0	990

Table 7. Sixty six (66) elementary reactions for C [22]

Tablica 7. Šezdeset šest (66) elementarnih reakcija ugljika C [22]

	Pre-exponential factor/Faktor k_0 (cm, K, s, mol)	Temperature index/ Temperaturni indeks β	Activation energy/ Aktivacijska energija E_a (cal/mol)
C(S)+2H_2<=>CH_4	1.62E+12	0	46822.7
C+H_2=>CH+H	1.90E+14	0	66889.6
C+H_2<=>CH_2	7.89E+13	0	160.057
C+CH_2=>CH+CH	8.91E+12	1.79	1667.46
CH<=>C+H	1.21E+14	0.15	0
CH+H=>C+H_2	1.00E-01	0	0
CH+H_2=>CH_2+H	9.00E-01	0	0
CH+H_2=>CH_3	1.20E+14	0	0
CH+CH=>C+CH_2	1.02E+13	0	0
CH+CH<=>C_2H+H	7.83E+13	0	0
CH+CH<=>C_2H_2	5.62E+15	0	89580.3
CH+CH_4<=>C_2H_4+H	6.02E+12	0	-1787.63
CH+C_2H_6<=>C_2H_4+CH_3	3.01E+09	0	0
CH_2<=>CH+H	2.40E+14	0	9930.72
CH_2+H=>CH+H_2	2.00E+14	0	10984.2
CH_2+H_2=>CH_3+H	1.58E+15	0	11937.4
CH_2+CH_2<=>CH_3+CH	2.00E+13	0	0
CH_2+CH_2<=>C_2H_2+H+H	1.26E+14	0	0
CH_2+CH_2<=>C_2H_2+H_2	1.81E+05	0	0
CH_2+CH_2<=>C_2H_3+H	4.30E-01	0	0
CH_2+CH_3<=>C_2H_4+H	1.81E+13	0	0
CH_2+CH_4=>CH_3+CH_3	1.81E+13	0	0
CH_2+CH_4<=>C_2H_6	1.81E+13	0	0
CH_2+C_2H<=>C_2H_2+CH	6.44E+12	0	7904.92
CH_2+C_2H_3<=>C_2H_2+CH_3	1.99E+23	-5.31	117057
CH_2+C_2H_5<=>C_2H_4+CH_3	5.00E+15	0	85045.4
CH_2+C_2H_6<=>C_2H_5+CH_3	6.02E+13	0	15095.56
CH_3<=>CH_2+H	2.37E+19	-2.17	0
CH_3=>CH+H_2	3.06E+10	2.7	8841.38
CH_3+H=>CH_2+H_2	4.30E+12	0	10031.1
CH_3+H=>CH_4	1.00E+11	0	0
CH_3+H_2=>CH_4+H	2.40E+13	0	12871.5
CH_3+CH_3=>CH_2+CH_4	1.62E+12	0	46822.7
CH_3+CH_3<=>C_2H_4+H_2	1.90E+14	0	66889.6

$CH_3+CH_3=>C_2H_5+H$	7.89E+13	0	160.057
$CH_3+CH_3<=>C_2H_6$	4.47E+13	-0.69	174.391
$CH_3+CH_4<=>C_2H_5+H_2$	1.00E+13	0	23041.1
$CH_3+CH_4=>C_2H_6+H$	6.32E+01	0	0
$CH_3+C_2H_2=>CH_4+C_2H$	1.81E+11	0	17281.4
$CH_3+C_2H_3<=>CH_4+C_2H_2$	1.81E+13	0	0
$CH_3+C_2H_4=>CH_4+C_2H_3$	4.16E+12	0	11122.8
$CH_3+C_2H_5<=>CH_4+C_2H_4$	1.36E+10	2.45	-2919.26
$CH_3+C_2H_6=>CH_4+C_2H_5$	1.05E+08	6	6039.18
$CH_4=>CH_3+H$	7.53E+23	-3.73	106463
$CH_4+H=>CH_3+H_2$	2.63E+11	3.16	8751.55
$CH_4+C_2H=>CH_3+C_2H_2$	5.15E+11	2.34	-754.897
$CH_4+C_2H_3=>CH_3+C_2H_4$	1.28E+10	4.02	5461.06
$CH_4+C_2H_5=>CH_3+C_2H_6$	1.51E+09	4.14	12553.8
$C_2H+H<=>C_2H_2$	1.39E+14	0.32	0
$C_2H+H_2=>C_2H_2+H$	5.39E+11	2.57	258.0029
$C_2H_2+H<=>C_2H_3$	6.50E-02	-7.27	7209.747
$C_2H_2+H=>C_2H+H_2$	6.02E+13	0	22245.58
$C_2H_2+H_2=>C_2H_3+H$	2.41E+12	0	64978.5
$C_2H_2+H_2<=>C_2H_4$	3.01E+11	0	38939.32
$C_2H_3+H=>C_2H_2+H_2$	1.21E+13	0	0
$C_2H_3+H<=>C_2H_4$	1.22E+14	0.2	0
$C_2H_3+H_2=>C_2H_4+H$	2.04E+10	2.56	5026.278
$C_2H_4+H<=>C_2H_5$	7.53E+12	1.07	1450.072
$C_2H_4+H=>C_2H_3+H_2$	1.26E+05	2.75	11643.57
$C_2H_4+H_2=>C_2H_5+H$	1.02E+13	0	68084.09
$C_2H_4+H_2<=>C_2H_6$	1.10E+03	0	0
$C_2H_5+H=>CH_3+CH_3$	3.61E+13	0	0
$C_2H_5+H=>C_2H_4+H_2$	1.81E+12	0	0
$C_2H_5+H<=>C_2H_6$	1.35E+14	0.16	0
$C_2H_6+H<=>C_2H_5+H_2$	2.68E+07	1.98	6321.07
$C_2H_6+H=>CH_4+CH_3$	5.40E+04	0	11619.68

Table 8. Seven (7) elementary reactions for S [23-27]

Tablica 8. Sedam (7) elementarnih reakcija sumpora S [23-27]

	Pre-exponential factor/Faktor k_0 (cm, K, s, mol)	Temperature index/ Temperaturni indeks β	Activation energy/ Aktivacijska energija E_a (cal/mol)
S+H+M<=>SH+M	2.03E+15	-0.6	0
$S+H_2=>SH+H$	1.35E+14	0	19285.71
$SH+H=>S+H_2$	1.02E+13	0	0
$SH+SH<=>S+H_2S$	2.41E+13	0	0
$H_2S<=>H_2+S$	4.00E+14	0	65456.28
$H_2S<=>H+SH$	1.76E+16	0	66172.96
$H_2S+H<=>H_2+SH$	1.10E+12	2.44	468.2274

Table 9. Twelve (12) elementary reactions for N [22, 28]

Tablica 9. Dvanaest (12) elementarnih reakcija dušika N [22,28]

	Pre-exponential factor/Faktor k_0 (cm, K, s, mol)	Temperature index/ Temperaturni indeks β	Activation energy/ Aktivacijska energija E_a (cal/mol)
$N_2+3H_2+M<=>2NH_3+M$	5E+14	0.25	17500
$NH+N<=>N_2+H$	1.500E+13	0.000	0.00
$NNH<=>N_2+H$	3.300E+08	0.000	0.00
$NNH+M<=>N_2+H+M$	1.300E+14	-0.110	4980.00
HCN+M<=>H+CN+M	1.040E+29	-3.300	126600.00
$H+HCN(+M)<=>H_2CN(+M)$	3.300E+13	0.000	0.00
H2CN+N<=>N2+CH2	6.000E+13	0.000	400.00
C+N2<=>CN+N	6.300E+13	0.000	46020.00
CH+N2<=>HCN+N	3.120E+09	0.880	20130.00

CH2+N2<=>HCN+NH	1.000E+13	.000	74000.00
NNH+H<=>H2+N2	5.000E+13	.000	.00
NNH+CH3<=>CH4+N2	2.500E+13	.000	.00

3.2. Validation of kinetics mechanism

Simulation results are compared with the published data for Datong Coal hydro-gasification in a hydro-gasifier. The pulverized coal was fed at a value of 1.2 g/min in the experiment [30]. N_2 was used as the protective gas and it was also used to sustain the reaction pressure in the gasifier. The analysis result of Datong coal is listed in Table 10 and species mole fractions in the input reactant mixture are listed in Table 11 with a value of U of 0.4. As shown in Figs. 8-10, the simulation results are in good agreement with the published data [30]. The maximum and minimum relative errors of the calculation results in Fig. 8 are 22.2% and 0.42% respectively. The maximum and minimum relative errors of the calculation results in Fig. 9 are 25.0% and 0.67% respectively. The maximum and minimum relative errors of the calculation results in Fig. 10 are 17.6% and 2.9% respectively. When studying the influences of T_R on the gasification process, only the carbon conversion ratio defined as the methane to carbon mass ratio [30] is shown in Fig. 10. Therefore, only the results of the carbon conversion ratio are compared in this work.

Table 10. Analysis result of Datong coal

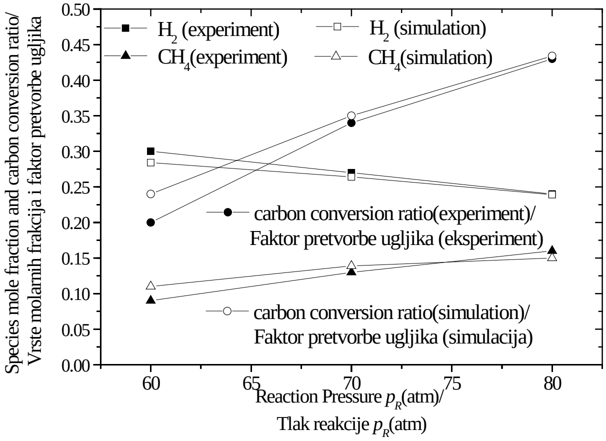
Tablica 10. Analiza rezultata objavljenih u „Dantog coal“

Proximate analysis/Neposredna analiza				Ultimate analysis/Konačna analiza				
Ash/Pepeo	Moisture/Vlaga	Volatile/Volatili	Carbon/Ugljik	C	H	O	N	S
0.06	0.002	0.3714	0.5666	0.8059	0.0463	0.1326	0.0070	0.0082

Table 11. Species mole fraction of reactant mixture

Tablica 11. Molarne frakcije vrsta reaktanata u mješavini

Species/Kemijske vrste	Hg	Cl	C(S)	H	O	N	S	H_2	H_2O	N_2
Mole fraction/Molarna frakcija	2.37E-9	3.34E-5	1.49E-1	1.03E-1	1.84E-2	1.11E-3	5.69E-4	4.74E-1	2.63E-4	2.54E-1



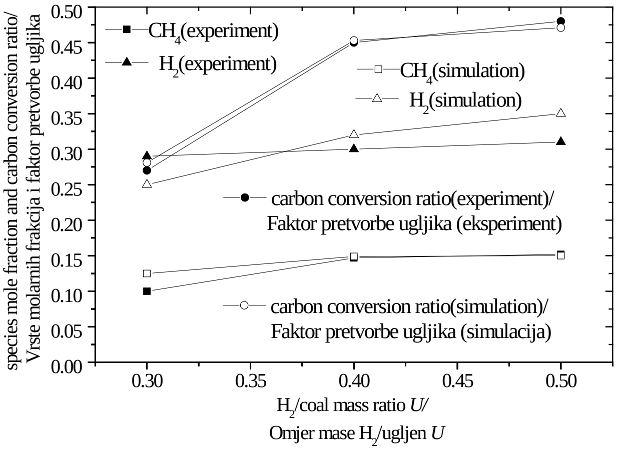


Figure 8. Effects of p_R on species mole fraction of gasification products and carbon conversion ratio with U of 0.4 and T_R of 800°C

Slika 8. Utjecaj p_R na molarne frakcije vrsta produkata rasplinjavanja i faktor pretvorbe ugljika uz U=0.4 i T_R =700°C

Figure 9. Effects of U on species mole fraction of gasification products and carbon conversion ratio with T_R of 700°C and p_R of 70 atm

Slika 9. Utjecaj U na molarne frakcije vrsta produkata rasplinjavanja i faktor pretvorbe ugljika uz T_R =700°C i p_r=70 atm

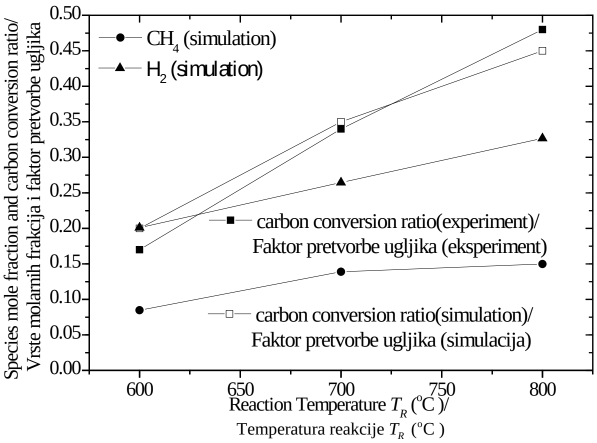


Figure 10. Effects of T_R on species mole fraction of gasification products and carbon conversion ratio with *U* of 0.4 and p_R of 70 atm

Slika 10. Utjecaj T_R na molarne frakcije vrsta produkata rasplinjavanja i faktor pretvorbe ugljika uz U=0.4 i p_R =70 atm

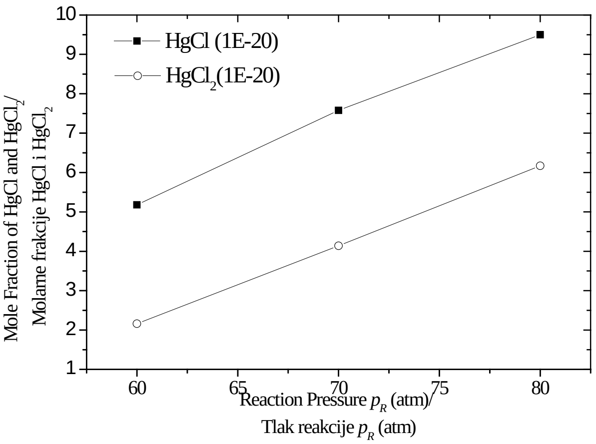


Figure 11. Effects of p_R on mercury specific transformation with *U* of 0.4 and T_R of 700°C

Slika 11. Utjecaj p_R na transformaciju žive uz U=0.4 i T_R =700°C

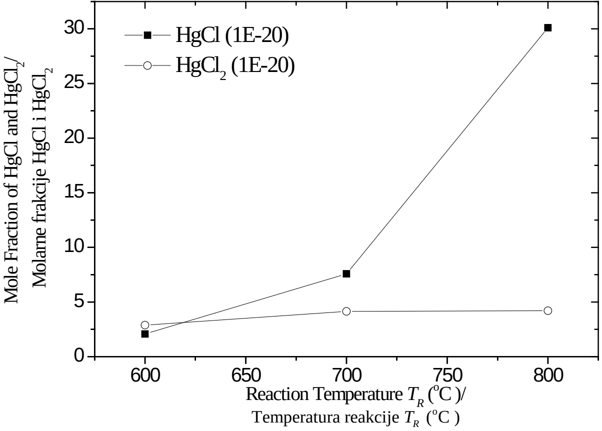


Figure 12. Effects of T_R on mercury specific transformation with *U* of 0.4 and p_R of 70 atm

Slika 12. Utjecaj T_R na transformaciju žive uz U=0.4 i p_R =70 atm

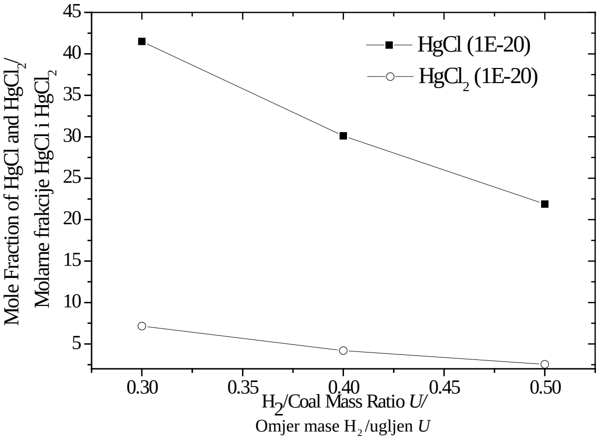


Figure 13. Effects of *U* on mercury specific transformation with T_R of 700°C and p_R of 70 atm

Slika 13. Utjecaj U na transformaciju žive uz T_R =700°C i p_R =70 atm

After validated, the kinetic mechanism and ChemKin 4.0 are used to predict the influences of T_R, p_R and *U* on mercury transformation. The influences of these three parameters on coal hydro-gasification products were shown in Figs. 8-10 by the experiment [30] and in the simulation results of this paper. The effects of these parameters on the coal hydro-gasification products and the mercury transformation process are shown in Figs. 8-13 when the detailed reaction kinetic mechanisms are used in the simulation.

The influences of reaction pressure p_R on gasification products and the carbon conversion ratio are shown in Fig. 8. The ole fraction of CH_4 and the carbon conversion ratio increase with the increase of p_R, and mole fraction of H_2 decreases when p_R increases. As it is known to all, species concentration increases when p_R increases. According to the mass action law, the reaction rate increases with the increase of species concentration. So the reaction rate increases as the p_R increases. The influences of the H_2/coal mass ratio *U* on gasification products and the carbon conversion ratio are shown in Fig. 9. The H_2 mole fraction, the CH_4 mole fraction and the carbon conversion ratio increase when *U* increases due to the increase of H_2 concentration. When *U* is greater than 0.4, it has a mild effect on the gasification products. The influences of the reaction temperature T_R on gasification products and the carbon conversion ratio are shown in Fig. 10. The carbon conversion ratio, H_2 and CH_4 mole fractions increase as T_R increases. Since the coal flow rate was set to a constant value of 1.2 g/min, the H_2 mass flow rate was also constant when *U* was set to a fixed value. Therefore, the amount of N_2 used to keep the reaction pressure decreases as T_R increases. The mole fraction of CH_4 and H_2 then increases with the increase of T_R. In addition, it can be concluded that the reaction in the experiment is still far from equilibrium due to the low carbon conversion ratio. Therefore, an increase of T_R will increase the reaction rate and finally increase the carbon conversion ratio, although the methane formation reaction is an exothermic reaction.

Mercury in gasification products is almost entirely gaseous Hg (g), except for a little amount of HgCl and $HgCl_2$. The influences of p_R, T_R and U on mercury transformation are shown in Figs. 11-13. Both the mole fractions of HgCl and $HgCl_2$ increase with the increase of p_R due to the increase of species concentration. The mole fraction of HgCl and $HgCl_2$ will both increase as T_R increases due to the increase of the reaction rate. When T_R is higher than 700°C, the mole fraction of HgCl will increase quickly as T_R increases. The mole fraction of HgCl and $HgCl_2$ will both decrease as U increases due to the dilution effect and the reducing action of excessive H_2.

4. Conclusions

Hydro-gasification of pulverized coal is the major part of the ZEC system. Well understanding the coal hydro-gasification characteristics and mercury transformation process at high pressure and high temperature is very important to the study of the performance of the whole ZEC system. Both chemical equilibrium calculation (CEC) and chemical kinetic mechanism (CKM) are used in this work to explore the coal hydro-gasification characteristics and mercury transformation process. The main points can be summarised as:

(1) The CEC model can properly reflect the hydro-gasification process of coal if the reaction time is maintained long enough. It is not appropriate to predict the gasification for the practical industry production because the actual reaction time is not long and the reactions are far from chemical equilibrium.
(2) The CKM model can properly reflect the actual hydro-gasification process. Further improvements still desired for this work are only done with the assumption of a homogeneous mechanism.
(3) Both the CEC and CKM models predict successfully that the main existing form of mercury in an entrained flow hydro-gasifier is as a gaseous element.
(4) Both the CEC and CKM models predict that an increase of pressure will both increase the progress of mercury oxidation and the conversion ratio of carbon.
(5) Both the CEC and CKM models predict that the oxidation of mercury will be restrained and the gasification will be promoted with the increase of the H_2/Coal ratio.

The CEC model predicts that increasing the reaction temperature will restrain the oxidation of mercury and the progress of gasification while the CKM model suggests that increasing the reaction temperature will promote the oxidation of mercury, and the gasification will be accelerated. The CKM results are believed to have practical guidelines since the reaction rate is taken into simulation.

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