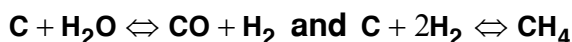


The Model for Theoretical Determination of Composition of a Heterogeneous Equilibrium Mixture in the Course of Chemical Reactions



Slavko Djurić

Technical College
Doboj, Republic Serpska

Miloš Kuburović

Professor

University of Belgrade
Faculty of Mechanical Engineering

Aleksandar Jovović

Assistant

University of Belgrade
Faculty of Mechanical Engineering

The work presents a new way of calculation of the composition of a heterogeneous equilibrium mixture in the course of chemical reactions important in engineering practice: soot production, coal gasification, waste pyrolysis, refining flue gases by dry and semi-dry treatments. In the available literature, the calculation of equilibrium composition of only the homogeneous (gaseous) phase is applied. This work presents three ways of calculation: based upon the number of moles, based upon the sum of the number of moles, and the calculation of the composition of only the homogeneous mixture. The reactions $\text{C} + \text{H}_2\text{O} \rightleftharpoons \text{CO} + \text{H}_2$ and $\text{C} + 2\text{H}_2 \rightleftharpoons \text{CH}_4$ have been considered, since in the available reference literature there is the largest number of data on the composition of the equilibrium homogeneous mixture concerning these reactions. The results of the calculation of the composition of the homogeneous (gaseous) phase, as a part of a heterogeneous mixture are identical with the results obtained by the orthodox calculation of only the homogeneous phase.

Keywords: chemical equilibrium, content of the solid phase, model.

1. INTRODUCTION

The calculation of content of the solid phase in the course of heterogeneous chemical reactions are important for a great number of processes: waste material treatment by applying the pyrolysis procedure, soot production, coal gasification, and flue gas treatment. In the available reference literature neither methodology nor results of calculation of the solid phase content in the equilibrium mixture can be found. The derived expressions refer solely to chemical reactions in the gaseous mixture [1], with note that the equilibrium constant applies both to homogeneous and heterogeneous equilibrium mixtures. In the heterogeneous reactions the Law on the effect of masses takes simplified form mostly, i.e. in the heterogeneous mixtures the pressure and the concentration of solid phase components need not to be taken into account [2]. However, there are processes in which it is necessary to determine the content of the solid component in the equilibrium mixture.

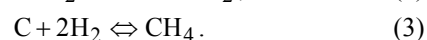
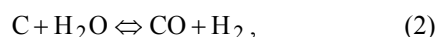
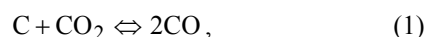
In heterogeneous reactions the chemical potentials of solid components remain constant independently on the degree of the course of the reaction. The necessary condition is that these components should not be

consumed until the chemical equilibrium has been established [3]. The model offered in these paper gives an answer to what conditions (pressure, temperature, initial components concentration) the solid phase components are completely consumed.

Since the content of the solid phase in the heterogeneous mixture is determined only by measuring it [4], the importance of the present paper is best supported by this reason of devising such a model. In order to satisfy the material balance of the chemical reaction, the solid phase must also be taken into account in the calculation of the reaction products.

2. THE CALCULATION METHODOLOGY

By calculating we assume that reactions occur by solid fuel gasification [5]:



The calculation methodology of content of the equilibrium mixture of the reaction (1) is shown in the available literature [6].

The following three methods of the content calculation are shown in this paper:

- calculation based upon the number of moles,
- calculation based upon the sum of the number of moles, and
- calculation of compositions of only homogeneous mixture.

The calculation of only a homogeneous mixture is well known and it can be found in the literature [7]. In

Received: June 2001, accepted: March 2002.

Correspondence to:

Aleksandar Jovović, Faculty of Mechanical Engineering,
Department of Process Engineering
27. marta 80, 11000 Belgrade, Yugoslavia

E-mail: pt.ajovovic@alfa.mas.bg.ac.yu

this paper the reaction $C + H_2O \rightleftharpoons CO + H_2$ and $C + 2H_2 \rightleftharpoons CH_4$ is considered.

2.1. The calculation based upon the number of kilomoles

In the course of reactions $C + H_2O \rightleftharpoons CO + H_2$ and $C + 2H_2 \rightleftharpoons CH_4$ the number of kilomoles of the components in the mixture after the chemical equilibrium has been established amounts to:

- for the reaction (2)

$$\text{Carbon: } n_C^{(2)} = a_2 - z_2, \quad (4)$$

$$\text{Water vapor: } n_{H_2O}^{(2)} = b_2 - z_2, \quad (5)$$

$$\text{Carbon-monoxide: } n_{CO}^{(2)} = z_2, \quad (6)$$

$$\text{Hydrogen: } n_{H_2}^{(2)} = z_2, \quad (7)$$

- for the reaction (3)

$$\text{Carbon: } n_C^{(3)} = a_3 - z_3, \quad (8)$$

$$\text{Hydrogen: } n_{H_2}^{(3)} = c_3 - 2z_3, \quad (9)$$

$$\text{Methane: } n_{CH_4}^{(3)} = z_3, \quad (10)$$

where: a_2, a_3 - number of carbon kilomoles taking part in the reactions (2) and (3) respectively, b_2 - number of water vapor kilomoles taking part in the reaction (2), c_3 - number of hydrogen kilomoles taking part in the reaction (3), z_2 - number of carbon-monoxide (hydrogen) kilomoles in the mixture after the chemical equilibrium has been established the reaction (2), z_3 - number of methane kilomoles in the mixture after the chemical equilibrium has been established the reaction (3).

The total number of kilomoles in the mixture after the chemical equilibrium has been established are following:

heterogeneous mixture (solid and gaseous phases):

- for the reaction (2)

$$n(s)^{(2)} = n_C^{(2)} + n_{H_2O}^{(2)} + n_{CO}^{(2)} + n_{H_2}^{(2)},$$

$$n(s)^{(2)} = (a_2 - z_2) + (b_2 - z_2) + z_2 + z_2 = a_2 + b_2, \quad (11)$$

- for the reaction (3)

$$n(s)^{(3)} = n_C^{(3)} + n_{H_2}^{(3)} + n_{CH_4}^{(3)},$$

$$n(s)^{(3)} = (a_3 - z_3) + (c_3 - 2z_3) + z_3 = a_3 + c_3 - 2z_3, \quad (12)$$

homogeneous mixture (gaseous phase only):

- for the reaction (2)

$$n(g)^{(2)} = n_{H_2O}^{(2)} + n_{CO}^{(2)} + n_{H_2}^{(2)},$$

$$n(g)^{(2)} = (b_2 - z_2) + z_2 + z_2 = b_2 + z_2. \quad (13)$$

- for the reaction (3)

$$n(g)^{(3)} = n_{H_2}^{(3)} + n_{CH_4}^{(3)},$$

$$n(g)^{(3)} = (c_3 - 2z_3) + z_3 = c_3 - z_3. \quad (14)$$

The mole contents of the components in the mixture after the chemical equilibrium of reactions (2) and (3) has been established amounts to:

heterogeneous mixture:

- for the reaction (2)

$$x_C = \frac{n_C^{(2)}}{n(s)^{(2)}} = \frac{a_2 - z_2}{a_2 + b_2}, \quad (15)$$

$$x_{H_2O} = \frac{n_{H_2O}^{(2)}}{n(s)^{(2)}} = \frac{b_2 - z_2}{a_2 + b_2}, \quad (16)$$

$$x_{CO} = \frac{n_{CO}^{(2)}}{n(s)^{(2)}} = \frac{z_2}{a_2 + b_2}, \quad (17)$$

$$x_{H_2} = \frac{n_{H_2}^{(2)}}{n(s)^{(2)}} = \frac{z_2}{a_2 + b_2}, \quad (18)$$

Nomenclature

a_2	[kmol]	- number of C kilomoles entering the reaction (2),
a_3	[kmol]	- number of C kilomoles entering the reaction (3),
b_2	[kmol]	- number of H_2O kilomoles entering the reaction (2),
c_3	[kmol]	- number of H_2 kilomoles entering the reaction (3),
n	[kmol]	- number of kilomoles in the equilibrium mixture,
K_{p2}	[Pa]	- chemical equilibrium constant of the reaction $C + H_2O \rightleftharpoons CO + H_2$,
K_{p3}	[Pa ⁻¹]	- chemical equilibrium constant of the reaction $C + 2H_2 \rightleftharpoons CH_4$,
K_p'	[-]	- chemical equilibrium constant of the reactions (2) and (3) reduced to pressure of 101300 Pa,
p	[Pa]	- pressure,

x	$\left[\frac{\text{kmol}}{\text{kmol}}\right]$	- mole content of the component in the heterogeneous equilibrium mixture (solid and gaseous phase),
y	$\left[\frac{\text{kmol}}{\text{kmol}}\right]$	mole content of the component in the homogeneous equilibrium mixture (gaseous phase),
z_2	[kmol]	- number of kilomoles in the equilibrium mixture, number of CO and H_2 kilomoles in the equilibrium mixture after the chemical equilibrium has been established the reaction (2),
z_3	[kmol]	- number of kilomoles in the equilibrium mixture, number of CH_4 kilomoles in the equilibrium mixture after the chemical equilibrium has been established the reaction (3).

Subscripts

C	- carbon,	CH_4	- methane,
CO	- carbon-monoxide,	H_2	- hydrogen,
g	- gaseous,	s	- solid,
I, J, M	- supplementary value.		

- for the reaction (3)

$$x_C = \frac{n_C^{(3)}}{n(s)^{(3)}} = \frac{a_3 - z_3}{a_3 + c_3 - 2z_3}, \quad (19)$$

$$x_{H_2} = \frac{n_{H_2}^{(3)}}{n(s)^{(3)}} = \frac{c_3 - 2z_3}{a_3 + c_3 - 2z_3}, \quad (20)$$

$$x_{CH_4} = \frac{n_{CH_4}^{(3)}}{n(s)^{(3)}} = \frac{z_3}{a_3 + c_3 - 2z_3}, \quad (21)$$

homogeneous mixture:

- for the reaction (2)

$$y_{H_2O} = \frac{n_{H_2O}^{(2)}}{n(g)^{(2)}} = \frac{b_2 - z_2}{b_2 + z_2}, \quad (22)$$

$$y_{CO} = \frac{n_{CO}^{(2)}}{n(g)^{(2)}} = \frac{z_2}{b_2 + z_2}, \quad (23)$$

$$y_{H_2} = \frac{n_{H_2}^{(2)}}{n(g)^{(2)}} = \frac{z_2}{b_2 + z_2}, \quad (24)$$

- for the reaction (3)

$$y_{H_2} = \frac{n_{H_2}^{(3)}}{n(g)^{(3)}} = \frac{c_3 - 2z_3}{c_3 - z_3}, \quad (25)$$

$$y_{CH_4} = \frac{n_{CH_4}^{(3)}}{n(g)^{(3)}} = \frac{z_3}{c_3 - z_3}. \quad (26)$$

The partial pressures of the components in the homogeneous mixture (gaseous phase) after the chemical equilibrium has been established are:

- for the reaction (2)

$$p_{H_2O} = y_{H_2O} p = \frac{b_2 - z_2}{b_2 + z_2} p, \quad (27)$$

$$p_{CO} = y_{CO} p = \frac{z_2}{b_2 + z_2} p, \quad (28)$$

$$p_{H_2} = y_{H_2} p = \frac{z_2}{b_2 + z_2} p, \quad (29)$$

- for the reaction (3)

$$p_{H_2} = y_{H_2} p = \frac{c_3 - 2z_3}{c_3 - z_3} p, \quad (30)$$

$$p_{CH_4} = y_{CH_4} p = \frac{z_3}{c_3 - z_3} p, \quad (31)$$

where p is the total pressure in the reactor space after the chemical equilibrium of the reactions (2) and (3) has been established.

The chemical equilibrium constant of the reactions (2) and (3) is defined by expression:

$$K_{p_2} = \frac{p_{CO} \cdot p_{H_2}}{p_{H_2O}} = p \frac{z_2^2}{b_2^2 - z_2^2}, \quad (32a)$$

$$K_{p_3} = \frac{p_{CH_4}}{p_{H_2}^2} = \frac{1}{p} \cdot \frac{z_3 \cdot (c_3 - z_3)}{(c_3 - 2z_3)^2}. \quad (32b)$$

By solving equation (32a) and (32b) at given $a_2, a_3, b_2, c_3, p, K_{p_2}, K_{p_3}$ is obtain the unknown values:

$$z_2 = \pm b_2 \sqrt{K_{p_2} / (p + K_{p_2})}, \quad (33)$$

and

$$z_3 = \frac{c_3}{2} (1 \pm 1 / \sqrt{1 + 4p K_{p_3}}). \quad (34)$$

2.2. The calculation based upon the sum of the number of kilomoles

For heterogeneous mixture after the chemical equilibrium has been established, in the course of the reactions $C + H_2O \leftrightarrow CO + H_2$ and $C + 2H_2 \leftrightarrow CH_4$ the following dependencies hold:

- for the reaction (2): the above stated expressions (27), (28) and (29),

- for the reaction (3): the above stated expressions (30) and (31),

- for the reaction (2)

$$x_C + x_{H_2O} + x_{CO} + x_{H_2} = 1, \quad (35a)$$

$$\frac{\sum C}{\sum H_2} = \frac{x_C + x_{CO}}{x_{H_2O} + x_{H_2}} = I, \quad (35b)$$

$$\frac{\sum C}{\sum O_2} = \frac{x_C + x_{CO}}{\frac{1}{2}x_{H_2O} + \frac{1}{2}x_{CO}} = J, \quad (35c)$$

$$K_{p_2} = \frac{p_{CO} p_{H_2}}{p_{H_2O}} = p \frac{x_{CO} x_{H_2}}{x_{H_2O} (1 - x_C)}, \quad (35d)$$

- for the reaction (3)

$$x_C + x_{H_2} + x_{CH_4} = 1, \quad (36a)$$

$$\frac{\sum C}{\sum H_2} = \frac{x_C + x_{CH_4}}{x_{H_2} + 2x_{CH_4}} = M, \quad (36b)$$

$$K_{p_3} = \frac{p_{CH_4}}{p_{H_2}^2} = \frac{1}{p} \frac{x_{CH_4} \cdot (1 - x_C)}{x_{H_2}^2}, \quad (36c)$$

where: $\sum C, \sum H_2, \sum O_2$ - the total number of kilomoles of carbon, hydrogen and oxygen respectively in the mixture before the chemical equilibrium has been set up, I, J, M - supplementary values.

The last equation of expression (35a-d) is obtained on the following way:

$$x_C + x_{H_2O} + x_{CO} + x_{H_2} = 1,$$

$$x_{H_2O} + x_{CO} + x_{H_2} = 1 - x_C,$$

$$p_{H_2O} + p_{CO} + p_{H_2} = p,$$

$$p_{H_2O} = \frac{x_{H_2O}}{1 - x_C} p; \quad p_{H_2} = \frac{x_{H_2}}{1 - x_C} p; \quad p_{CO} = \frac{x_{CO}}{1 - x_C} p,$$

$$y_{H_2O} = \frac{x_{H_2O}}{1 - x_C}; \quad y_{H_2} = \frac{x_{H_2}}{1 - x_C}; \quad y_{CO} = \frac{x_{CO}}{1 - x_C}.$$

The last equation of expression (36a-c) is obtained in the similar way. The solutions of the system of four equations (expressions (35a-d)) with four unknown values $x_C, x_{H_2O}, x_{CO}, x_{H_2}$ and the system of three equations (expression (36a-c)) with three unknown values x_C, x_{H_2}, x_{CH_4} are:

- for the reaction (2)

$$A x_C^2 + B x_C + C = 0, \quad (37)$$

$$x_{\text{H}_2\text{O}} = \frac{I(2-J)}{J(1+I)} + x_{\text{C}} ; x_{\text{CO}} = \frac{I}{1+I} - x_{\text{C}} , \quad (38),(39)$$

$$x_{\text{H}_2} = \frac{J+IJ-2I}{J(1+I)} - x_{\text{C}} , \quad (40)$$

where:

$$A = J(1+I)(p + K_{p_2}) ,$$

$$B = (p + K_{p_2})[I(2-J) - J(1+I)] ,$$

$$C = pIJ - K_{p_2}I(2-J) - \frac{2pI^2}{1+I} .$$

Values I and J have been based upon the conditions:

$$I = \frac{\sum C}{\sum H_2} = \frac{a_2}{b_2} , \quad (41a)$$

and

$$J = \frac{\sum C}{\sum O_2} = 2 \frac{a_2}{b_2} = 2I . \quad (41b)$$

- For the reaction (3)

$$x_{\text{C}} = \frac{1}{2M(4M^2pK_{p_3} + M^2 - 1)} [8M^3pK_{p_3} + 2M^3 - (M^2 - M)\sqrt{1+4pK_{p_3}} - (4pK_{p_3} - 1)M^2 - M] \quad (42a)$$

$$x_{\text{H}_2} = \frac{-1 + M\sqrt{1+4pK_{p_3}}}{M^2(1+4pK_{p_3}) - 1} , \quad (42b)$$

$$x_{\text{CH}_4} = \frac{1}{2M[M^2(1+4pK_{p_3}) - 1]} [4M^2pK_{p_3} - (M + M^2)(1 + \sqrt{1+4pK_{p_3}})] \quad (42c)$$

The value M has been based upon the condition:

$$M = \sum C / \sum H_2 = a_3 / c_3 \quad (43)$$

2.3. The calculation of the composition of a homogeneous mixture only

For homogeneous mixture after the chemical equilibrium has been established in the course of the reactions $\text{C} + \text{H}_2\text{O} \rightleftharpoons \text{CO} + \text{H}_2$ and $\text{C} + 2\text{H}_2 \rightleftharpoons \text{CH}_4$ the following dependencies hold:

- for the reaction (2)

$$p_{\text{H}_2\text{O}} = y_{\text{H}_2\text{O}} p ; p_{\text{CO}} = y_{\text{CO}} p , \quad (44),(45)$$

$$p_{\text{H}_2} = y_{\text{H}_2} p , \quad (46)$$

$$K_{p_2} = \frac{p_{\text{CO}} p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} = \frac{y_{\text{CO}} y_{\text{H}_2}}{y_{\text{H}_2\text{O}}} p , \quad (47)$$

$$y_{\text{H}_2\text{O}} + y_{\text{CO}} + y_{\text{H}_2} = 1 ; y_{\text{CO}} = y_{\text{H}_2} . \quad (48),(49)$$

Keeping in mind that initial concentrations are not considered, but only stoichiometry of the process - that constitutes a fault of this model (calculation) - it can be written: from expression (48) and (49) follows:

$$y_{\text{H}_2\text{O}} = 1 - 2y_{\text{CO}} , \quad (50)$$

from expression (47) follows:

$$K_{p_2} = \frac{y_{\text{CO}}^2}{1 - 2y_{\text{CO}}} p , \quad (51)$$

and there from:

$$y_{\text{H}_2\text{O}} = [p + 2K_{p_2} - 2\sqrt{K_{p_2}(p + K_{p_2})}] / p , \quad (52a)$$

$$y_{\text{CO}} = [-K_{p_2} + \sqrt{K_{p_2}(p + K_{p_2})}] / p , \quad (52b)$$

$$y_{\text{H}_2} = [-K_{p_2} + \sqrt{K_{p_2}(p + K_{p_2})}] / p , \quad (52c)$$

- for the reaction (3)

$$p_{\text{H}_2} = y_{\text{H}_2} p ; p_{\text{CH}_4} = y_{\text{CH}_4} p , \quad (53),(54)$$

$$K_{p_3} = \frac{p_{\text{CH}_4}}{p_{\text{H}_2}^2} = \frac{1}{p y_{\text{CH}_4}} ; y_{\text{H}_2} + y_{\text{CH}_4} = 1 . \quad (55),(56)$$

The solutions of the system of two equations (55) and (56) with two unknown values y_{H_2} and y_{CH_4} are:

$$y_{\text{H}_2} = \frac{-1 + \sqrt{1 + 4pK_{p_3}}}{2pK_{p_3}} , \quad (57a)$$

$$y_{\text{CH}_4} = \frac{1 + 2pK_{p_3} - \sqrt{1 + 4pK_{p_3}}}{2pK_{p_3}} . \quad (57b)$$

The value of the chemical equilibrium constant K_p is reduced to the pressure $p_o = 1.013 \cdot 10^5$ Pa and is thus determined by the expression:

$$K_p' = K_p / p_o^{\Delta n} , \quad (58)$$

whereby the numerical value of the change of the number of kilomoles in the gaseous phase in the course of the reactions is (2) and (3):

$$\Delta n_2 = b_{\text{CO}} + b_{\text{H}_2} - b_{\text{H}_2\text{O}} = 1 + 1 - 1 = 1 \text{ kmol} ,$$

$$\Delta n_3 = b_{\text{CH}_4} - b_{\text{H}_2} = 1 - 2 = -1 \text{ kmol} ,$$

$$K_{p_2} = K_{p_2}' p_o^{\Delta n_2} = K_{p_2}' p_o , \quad (59)$$

$$K_{p_3} = K_{p_3}' p_o^{\Delta n_3} = K_{p_3}' p_o^{-1} . \quad (60)$$

It is an interesting question at which value of dimension $I = \sum C / \sum H_2$ and $M = \sum C / \sum H_2$, at given temperature, in the equilibrium mixture the reactions (2) and (3) does not exist solid phase, i.e. $x_{\text{C}} = 0$. The answer can be obtained by using expression (37), (41) and, the first equation of expressions (42) and (43).

- for the reaction (2)

$$x_{\text{C}} = \frac{1}{4I(1+I)(p + K_{p_2})} [4I^2(p + K_{p_2}) - \sqrt{p + K_{p_2}} \times \sqrt{16I^4(p + K_{p_2}) - 16I^2(pI^2 - K_{p_2} + K_{p_2}I^2)}] \geq 0 . \quad (61)$$

The expression (61) is transformed to an equivalent expression:

$$x_{\text{C}} = \frac{I(p + K_{p_2}) - \sqrt{(p + K_{p_2})K_{p_2}}}{(1+I)(p + K_{p_2})} \geq 0 . \quad (62)$$

Since $1+I > 0$ and $p + K_{p_2} > 0$ unequation (62) is transformed to unequation:

$$I(p + K_{p_2}) - \sqrt{(p + K_{p_2})K_{p_2}} \geq 0 , \quad (63)$$

whose set of solutions is:

$$I \geq \frac{\sqrt{(p + K_{p_2})K_{p_2}}}{p + K_{p_2}} . \quad (64)$$

The set of solutions of unequation (64) is equivalent to the set of solutions of the starting unequation (61).

- for the reaction (3) (expression (42.a))

$$x_{\text{C}} \geq 0 . \quad (65)$$

The expression (65) is transformed to an equivalent expression:

$$\frac{M^2(M - \frac{1}{2} + 1/2\sqrt{1+4pKp_3})}{(1+4pKp_3)(M\sqrt{1+4pKp_3} + 1)} \geq 0 \quad (66)$$

Since $M > 0$ and $1+4pKp_3 > 0$ unequation (66) is transformed to inequation:

$$M - \frac{1}{2} + \frac{1}{2\sqrt{1+4pKp_3}} \geq 0 \quad (67)$$

whose set of solutions is:

$$M \geq \frac{1}{2}(1 - 1/\sqrt{1+4pKp_3}) \quad (68)$$

The set of solutions of inequation (68) is equivalent to the set of solutions of the starting inequation (65).

3. THE CALCULATION RESULTS

The model of theoretical determination of composition of a heterogeneous equilibrium mixture presented in this paper has been used several times and has been confirmed in solving practical engineering problems, such as: waste material treatment by applying pyrolysis procedure, coal gasification and treatment of flue gas. The numerical example has been devised with

the adopted values of the pressure of $p = 10^5$ Pa and the temperature of 773 K (500°C), so selected for the sake of comparison of the results obtained with the data quoted in the available literature.

At the temperature of 773 K the value of the chemical equilibrium constants of the reactions (2) and (3) are $K_{p_2}' = 0.021512$ and $K_{p_3}' = 2.2019$ [7]. By using expression (59) and (60), are obtain the values

$$K_{p_2} = 0.0218 \cdot 10^5 \text{ Pa}$$

and

$$K_{p_3} = 0.24 \cdot 2.2019 \cdot 1.013 \cdot 10^{-5} = 0.5218 \cdot 10^{-5} \text{ Pa}^{-1}$$

where is: 0.24-coefficient of constant chemical equilibrium of the reaction $C + 2H_2 \rightleftharpoons CH_4$ [5]. By substituting p and K_p for the numerical values in the expressions (64) and (68) are obtain conditions:

$$I \geq 0.146065 \text{ and } M \geq 0.215431 \quad (69)$$

At the values $I \leq 0.146065$ and $M \leq 0.215431$ and the temperature of 500°C the solid phase does not exist in the equilibrium mixture of the reactions (2) and (3) ($x_C = 0$).

Table 1. The contents of a heterogeneous and a homogeneous mixture of the reaction $C + H_2O \rightleftharpoons CO + H_2$ at temperature of 500°C

	Heterogeneous mixture				Homogeneous mixture		
	x_C	x_{H_2O}	x_{CO}	x_{H_2}	y_{H_2O}	y_{CO}	y_{H_2}
Calculation based upon the number of moles – expressions (15) to (21)							
$I=0.50$ $a_2=1$ kmol $J=1.00$ $b_2=2$ kmol	0.235957	0.569291	0.097376	0.097376	0.754102	0.127449	0.127449
$I=0.75$ $a_2=1$ kmol $J=1.50$ $b_2=1.33$ kmol	0.345106	0.487962	0.083466	0.083466	0.745102	0.127449	0.127449
$I=1.00$ $a_2=1$ kmol $J=2.00$ $b_2=1$ kmol	0.426968	0.426968	0.073032	0.073032	0.745102	0.127449	0.127449
Calculation based upon the sum of the number of moles - expressions (37) to (40)							
$I=0.50$ $J=1.00$	0.235957	0.569291	0.097376	0.097376	0.754102	0.127449	0.127449
$I=0.75$ $J=1.50$	0.345106	0.487962	0.083466	0.083466	0.745102	0.127449	0.127449
$I=1.00$ $J=2.00$	0.426968	0.426968	0.073032	0.073032	0.745102	0.127449	0.127449
Calculation of the composition of the homogeneous mixture only – expression (52)							
	-	-	-	-	0.745102	0.127449	0.127449

Table 2. The contents of a heterogeneous and a homogeneous mixture of thereaction $C + 2H_2 \rightleftharpoons CH_4$ at temperature of 500°C

	Heterogeneous mixture			Homogeneous mixture	
	x_C	x_{H_2}	x_{CH_4}	y_{H_2}	y_{CH_4}
Calculation based upon the number of moles – expressions (22) to (26)					
$M = 0.50$ $a_3 = 1$ kmol $c_3 = 2$ kmol	0.266167	0.532333	0.201500	0.725415	0.274585
$M = 1.00$ $a_3 = 1$ kmol $c_3 = 1$ kmol	0.500000	0.362707	0.137293	0.725415	0.274585
$M = 1.50$ $a_3 = 1$ kmol $c_3 = 0.66$ kmol	0.620823	0.275060	0.104117	0.725415	0.274585
Calculation based upon the sum of the number of moles – expression (42)					
$M = 0.50$	0.266167	0.532333	0.201500	0.725415	0.274585
$M = 1.00$	0.500000	0.362707	0.137293	0.725415	0.274585
$M = 1.50$	0.620823	0.275060	0.104117	0.725415	0.274585
Calculation of the composition of the homogeneous mixture only – expression (57)					
	-	-	-	0.725415	0.274585

Basing upon condition (69) the following values have been adopted for the analysis $I=0.5; 0.75; 1.0; a_2=1$ kmol (Table 1) and $M=0.5; 1.0; 1.5; a_3=1$ kmol (Table2). The value $I=1.0$ corresponds to stoichiometric relationship of C and H₂O for the reaction (2), and value $M=0.5$ corresponds to stoichiometric relationship of C and H₂ for the reaction (3). By increasing the number of carbon kilomoles in the initial components of the reaction (2) (the increase in value of I), the mole content of carbon (x_C) increases in the heterogeneous mixture, whereas the mole content of the components in the homogeneous mixture ($y_{H_2O}, y_{CO}, y_{H_2}$) does not change (Table 1).

By increasing the number of carbon kilomoles in the initial components of the reaction (3) (the increase in value of M), the mole content of carbon (x_C) increases in the heterogeneous mixture, whereas the mole content of the components in the homogeneous mixture (y_{H_2}, y_{CH_4}) does not change (Table 2).

The results determined by using expressions (15) to (21) and (22) to (26) (the calculation based upon the number of moles) are identical to the ones determined by using expressions (37) to (40) and (42) (the calculation based upon the relation of the sum of the number of moles). The composition of the homogeneous mixture determined by using expressions (19) to (26), and (52), (56), respectively, conforms to the results of the calculation of the homogeneous mixture presented in the available literature [7].

4. CONCLUSION

The presented model emerged from solutions to practical engineering problems (waste material treatment by applying the pyrolysis procedure, soot production, coal gasification, and flue gas treatment). For the sake of satisfying the material and thermal balance in heterogeneous systems, the solid phase content in the equilibrium mixture must be taken into account. At given relationship of the masses of the initial components there exists a definite temperature at which the solid phase ceases to exist in the equilibrium mixture. For the considered reactions, the following conditions can be established by utilising the model presented here. In course of particular chemical reactions the calculation is simpler if expressions (15) to (26) are used. With simultaneous reactions taking part in the reaction space the complexity of solving of the model according to expressions (15) to (26) is the same as according to expressions (37) to (42). The results of the calculation of the homogeneous (gaseous) phase, as a part of the heterogeneous mixture (expressions (15) to (26) and (37) to (42)), are identical

with results of the calculation of the homogeneous phase only (expressions (52) and (57)).

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ODREĐIVANJE RAVNOTEŽNOG STAŃA SASTAVA ХЕТЕРОГЕНЕ МЕШАВИНЕ ПРИ ОДВИЈАЊУ РЕАКЦИЈЕ $C + H_2O \rightleftharpoons CO + H_2$ И $C + 2H_2 \rightleftharpoons CH_4$

С. Ђурић, М. Кубуровић, А. Јововић

Рад представља нов начин израчунавања састава хетерогене равнотежне мешавине хемијских реакција важних у инжењерској пракси: производњи чађи, гасификацији угљева, пиролизи отпада, пречишћавању димних гасова сувим и полусувим поступцима. Рад описује три начина израчунавања и то: заснована на броју киломола, суми броја киломола и израчунавању састава само хомогене мешавине.