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## MODELING OF PARTIAL SEGMENTS IN THE PROCESS OF GASIFICATION OF AGRICULTURAL BIOMASS

### MODELIRANJE DELA PROCESA GASIFIKACIJE POLJOPRIVREDNE BIOMASE

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#### REZIME

Cilj prezentovanog rada je proučavanje gasifikacije i sagorevanja biomase i čvrstog otpadnog materijala. Iskustveno-eksperimentalni model bio je razvijen sa glavnim ciljem izračunavanja sastava gasa pri različitim radnim uslovima. Prezentovani model uzima u obzir nekoliko pretpostavki i daje pojednostavljen model za određivanje molarnog odnosa velikih gasnih komponenata na izlazu iz fluidizovanog sloja.

**Ključne reči:** modelovanje, gasifikacija, sagorevanje, fluidizovani sloj, biomasa, čvrsti otpadni materijal.

#### SUMMARY

The aim of the present work is to study the gasification and combustion of biomass and solid waste material. An empirically - experimental model was developed with the main objective of calculating the gas composition at different operating conditions. The present model takes into consideration few assumptions, and gives a simplified model for determination of the molar rates of tall gas components on the fluidized bed exit.

**Key words:** modeling, gasification, combustion, fluidized bed, biomass, solid waste material.

#### INTRODUCTION

According to the general theory of mathematical modeling [8], there are three ways for models developing: theoretical or analytical, experimental or empirical, and combined analytically experimental.

As far as their application is concerned [11], the gasification models may be used in process study (learning models), modification of the gasification process (development and design models), or data collection and elaborating (correlation models).

Also, the models can be classified in three different levels of representation [21]:

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- Models obtained by "microscopic" approach, which comprises the coupled equations of momentum, mass and heat transfer for the individual elementary segments of the system concerned. This approach allows complete qualitative description of all present processes and operations. In the meantime, since many parameters are not well known, the usage of these models for obtaining qualitative results is uncertain.

-The second approach describes the bed dynamics, transport phenomena and the chemical reactions with empirical relations - functions of the local conditions. This approach allows consideration of the coupled mechanisms with less calculation time than the first approach. The utilization of this approach laying simple experiments requires the determination of model parameters, which are not fundamental but "synthetic" parameters.

- The third approach bases on more simplified models which take account of only the controlling phenomena in different zones of the fluidized bed and they are based on a curve fitting from experimentally obtained data.

Actually, the theoretical model bases on the "microscopic" approach but it also uses experimental data for determination of the model parameters. For example, the kinetic counts in the individual differential equations, which define the kinetics of individual chemical reactions present in the analyzing process, are still experimentally determined. Because of that, the degree of breaking up the modeling process to elementary parts that will be described with separate relations is of great importance. Further more, these relations will be mutually and appropriately connected on integral level. Apart from the specific advantages, (such as the validity in wide range of variable varying), the theoretical models have also some disadvantages. One of them is based on the fact that the theoretical models are very complex and often (it is insolvable) or very hard to solve them and because of that they are unpractical [6, 12].

On the other hand, the analytically-experimental models penetrate into details and therefore their usage from the points of application and definition of global processes and operations is justified. This approach provides overview of the chemical nature of these processes and operations and at the same time keeping back the models validity for wide range of varying variables and parameters for the system concerned

Although, the empirical models may demonstrate the real situation in the best way, they are still limited with their validity only for gasifies for which they are carried out or for identical gasifies. Also, they are not able to stand the sensitivity test of parameters and variables varying in wide range [10, 5, 22].

Because of that, we will concentrate on the carrying out of analytically-experimental model for gasification process of biomass and solid waste material and the theoretical model will be used as a base for analytically-experimental model defining. Namely, with previous defining of the processes and operations present in the gasification process and marking of the mathematical instrument needed for this use, a logical base will be formed for indicating the range and trends for assumed simplifications. These assumptions lead to developing of credible and practical analytically-experimental model for gasification of biomass and solid waste material. This is a very well documented and tested procedure that consists of previous defined assumptions. These assumptions give opportunity to make the process of simplification possible and also marking of possible limitations, which are result of the assumptions [14, 20, 17, 18].

In the fluidized bed reactor the following processes and operations are present:

Fluid dynamics, coupled to the dynamics of the solid inert material particles (fluidized bed);  
Chemical reactions: pyrolysis reactions and reactions of combustion and gasification.

Operations of momentum, mass and energy transfer between particles of the solid and gaseous phase.

Modern trends in ecological engineering [13,9,12] and waste management [7, 2], encourage numerous researchers to study on : the charaterization [19], modeling [6, 12], application [15,3,16] and dimensionation of the plants [23,25], for gasification of different type of solid biomasses [3,24,12].

### Nomenclature

a = tar hydrogen atoms  
b = tar oxygen atoms  
 $C_i$  = molar number of i-species. obtained by termal cracking of tar  
 $d_c$  = char particles diameter  
 $k_a$  = apparent rate constant  
 $K_{aj}$  = adsorption constant of i-species  
 $K_{eq}$  = equilibrium constant of reaction  
p = pressure  
 $P_i$  = partial pressure of i-species  
T = temperature  
v = reaction rate  
w = molar number of injected water  
 $X_i$  = molar number of i-species  
 $X_{i,0}$  = initial molar number of i-species  
y = molar number of injected oxigen  
z = molar number of injected nytrogen  
Greek symbols  
 $\alpha$  = biomass hydrogen atoms  
 $\beta$  = biomass oxygen atoms  
 $\gamma$  = biomass carbon atoms  
 $\lambda$  = initial carbon/methane ratio  
 $\rho_c$  = char particles density,  
 $\omega$  = molar ratio of carbon monoxide to carbon dioxide

### Indexes

0 = initial	6 = nitrogen
1 = hydrogen	7 = water
2 = carbon monoxide	8 = tar
3 = methane	9 = carbon
4 = carbon dioxide	10 = oxygen
5 = ethylene	

## RESULTS AND DISCUSSION

### Dynamic of the material flows which participate in the gasification process

The fluid dynamics is connected with flow rate of the fluidization medium (usually air) through the inert bed (solid material) in down-up direction. There are a lot of models for bed fluid dynamics presentation.

One of them is a Modified Bubble Assemblage Model (MBAM) developed by Mori and Wen [1]. According to this model, the reaction part of the reactor is divided into two vertical compartments in the dense bed and in the freeboard zone (Fig. 1). Besides, there is another part for supply of fluidization medium - air compartment.

There are two phases into the fluidized bed: bubble phase and emulsion phase. The emulsion phase is assumed to contain all the solid particles plus the interstitial gas necessary to maintain it at minimum fluidizing conditions and the bubble phase contains excess air.

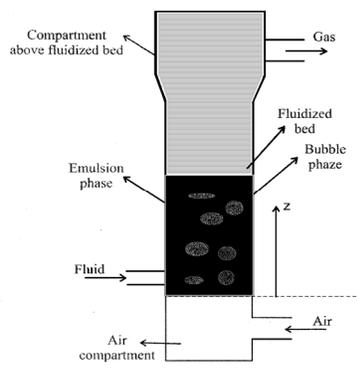


Fig. 1. Fluidized bed gasifier

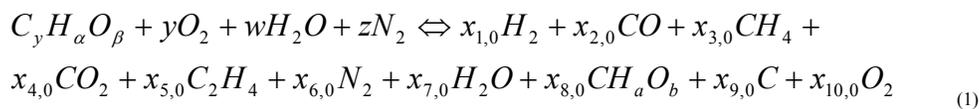
In the derivation of the mathematical model developed by theoretical approach, which will be presented in another study, in both phases of the fluidized bed (bubble and emulsion) and above the bed, uniformity is presumed of the physico-chemical, fluid dynamic conditions and temperature only into the radial direction. In the process of use this approach, theoretical, empirical and semi-empirical functional dependences into the vertical dimension are carried out for defining of local fluid dynamic conditions in and above the bed.

The simplified empirically - analytical model, which is represented in this work, postulates a "reaction box" with homogeneous, uniform physico-chemical conditions in all reactor directions [6]. The gasifier residence time is assumed as the time available for chemical processes and physical operations. This assumption is a great simplification for the model because allows excluding the fluid dynamics of the participants into the gasification process in the local level.

### Pyrolysis reactions

The second important assumption, which will be used for mathematical modeling, is instantaneous decomposing (pyrolysis) of the solid fuel particles with introducing of the fuel to the reactor. because of the high temperature there. The result of this thermal decomposition is a mixture of the specific gases (methane, ethylene, water vapor, carbon monoxide, hydrogen and tar) and coke in solid condition.

The global reaction of the instantaneous pyrolysis of biomass  $C\gamma H\alpha O\beta$  is the following:



The index 0 is related to the initial conditions of the oxidation and gasification reactions, i.e. to the moment of instantaneous pyrolysis.

In the moment of biomass pyrolytical decomposition, it can be assumed that:

- $X_{4,0} = 0$  because the quantity of oxygen present in the biomass is small and insufficient for carbon monoxide forming;
- $X_{6,0} = z$  where  $z$  represent the molar number of nitrogen added with the air which is introduced for partial biomass combustion; and
- $X_{10,0} = y$  where  $y$  represent the molar number of oxygen added with the air which is introduced for partial biomass combustion.

### Reactions of combustion and gasification

In the zone of fuel and air introduction, we can assume separate or simultaneous performance of combustion and gasification reactions.

The theoretical mathematical model postulates existing of two separate zones: combustion zone (oxygen depletion) and gasification zone. The schematic diagram of combustion and gasification model is presented in Fig. 2 and the contribution scheme of the individual material flows into the mass balances is represented in Fig. 3.

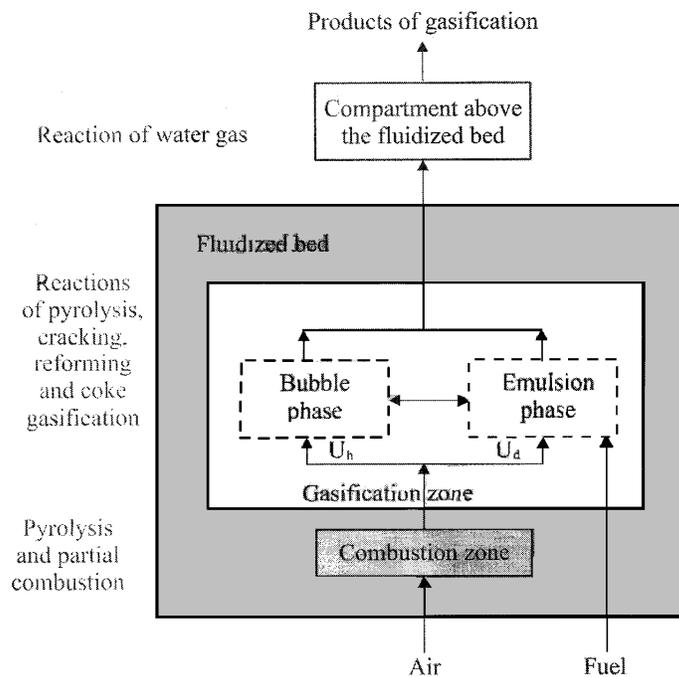


Fig. 2. A schematic diagram for the gasifier model

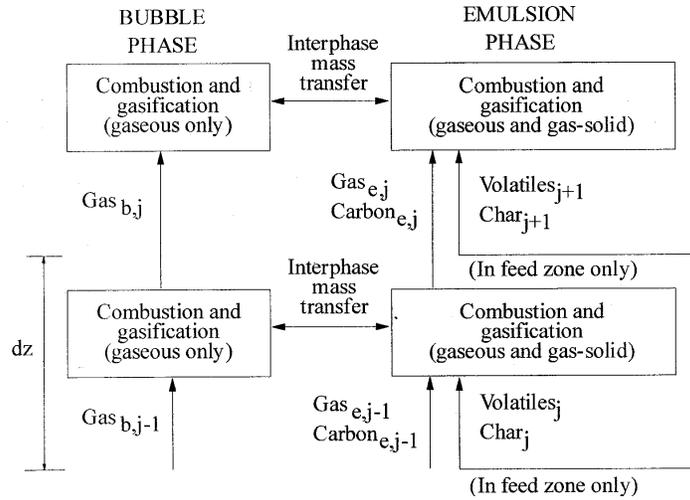
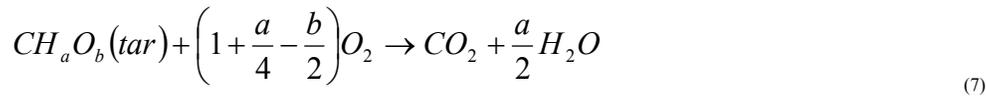
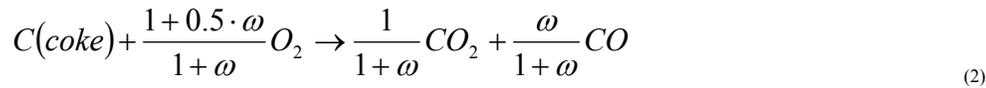


Fig. 3. Contribution of oxidation of the materia flows

The reactions of oxidation (combustion) are the following:



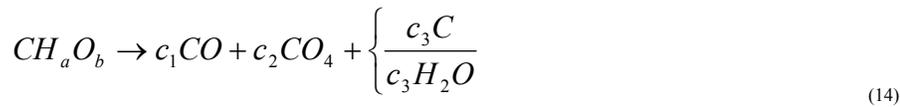
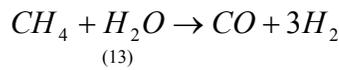
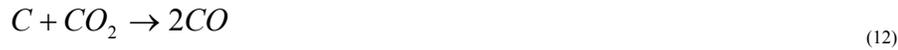
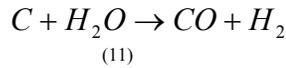
Reactions (3) - (7) occur into both bubble and emulsion phase, and the reaction of carbon oxidation - solid/gas reaction (2) occurs in emulsion phase only.

It is assumed that the combustion reactions are being carried out till all present oxygen is over. If the quantity of present oxygen is not enough for complete oxidation, carbon monoxide and hydrogen will oxidize into equivalent quantities first. Then, if oxygen is still present,  $CH_4$ ,  $C_2H_4$ ,  $CH_aO_b$  (tar) and finally carbon are oxidizing. The parameters a and b into the tar formula depends on the temperature, and the carbon monoxide/carbon dioxide molar ratio (parameter  $\omega$ ) is given by the expression:

$$\omega = 10^{3.4} \exp(-6241 \cdot T) \quad (8)$$

Where  $\omega$  is bed temperature [K]

The reactions of gasification and thermal creaking of the tar are given with followed expressions:



Where:

$$\text{for } 1 - \frac{a}{4} - b \geq 0 \Rightarrow c_1 = b; c_2 = \frac{a}{4}; c_3 = 1 - \frac{a}{4} - b;$$

$$\text{for } 1 - \frac{a}{4} - b < 0 \Rightarrow c_1 = \frac{(4 + 2b - a)}{6}; c_2 = \frac{[2 \cdot (1 - b) + a]}{6}; c_3 = \frac{[4 \cdot (b - 1) + a]}{6};$$

The reactions of combustion and gasification can be classified into two groups: reactions in gaseous medium - reactions (3), (4), (5), (6), (7), (9), (13) and (14); and reactions between solid and gaseous phase - reactions (2), (10), (11) and (12).

### Operations of monomentum, mass and heat transfer

Reactions occurring in the emulsion phase actually are reactions on the surface solid/gas where the solid is represented with the surface of the inert material particles into the fluidized bed (sand) except the reactions involving coke. For coke and emulsion phase, this boundary solid/gas is represented with the coke particle surface, which is actively involved into the present chemical reactions. During the reaction, coke is depleted and it has catalytic characteristic, too. This reaction model solid/gas is known as shrinking char model [2].

The phenomena on the border solid/gas can be divided into five sequential steps:

- Diffusion of reactants to the solid particle external surface through the surrounding stagnant film;

- Pore diffusion of gas inside the solid particles (only for coke particles);
- Adsorption, surface reaction, and de-sorption on the pore walls and/or on the particle external surface ;
- Diffusion of products outside the pores (only for coke particles) ; and
- Diffusion of products through the stagnant film.

The diffusion of reactants to the external particle surface through the stagnant film is controlled by the mass transfer correlation, and the amount of transferred mass is a weak function of the temperature and the relative flue gas-particles velocity. The mass transfer across the stagnant film is decreasing with increasing of the relative velocity and with decreasing of the particle size in particular, the mass transfer rate and the external surface area per unit weight are reverse proportional. This means that the mass transfer per unit weight decreases with increasing particle size, becoming a limiting rate factor for large size particles.

The simplified empirically-analytical model for pyrolytic decomposition, which is presented in this work, beside the initial conditions, also gives the following assumptions:

- $X_{5,0} = 0$ , because it is assumed that minimum quantities of ethylene are formed, and
- $X_{8,0} = 0$ , because it is assumed that the whole tar immediately pyrolyzed into gaseous products.

If we assume  $\lambda$  initial carbon/methane ratio, then the initial conditions, which correspond with occurring of reactions of pyrolytical decomposition (before the presence of oxygen is taken account), are the following:

$$x_{1,0} = \frac{\alpha - \beta}{2} - \frac{2}{1 + \lambda} \left( 1 - \frac{\beta}{2} \right) \quad (15)$$

$$x_{2,0} = \frac{\beta}{2} \quad (16)$$

$$x_{3,0} = \frac{1}{1 + \lambda} \left( 1 - \frac{\beta}{2} \right) \quad (17)$$

$$x_{4,0} = 0 \quad (18)$$

$$x_{5,0} = 0 \quad (19)$$

$$x_{6,0} = z \quad (20)$$

$$x_{7,0} = w + \frac{\beta}{2} \quad (21)$$

$$x_{8,0} = 0 \quad (22)$$

$$x_{9,0} = \frac{\lambda}{1 + \lambda} \left( 1 - \frac{\beta}{2} \right) \quad (23)$$

$$x_{10,0} = y \quad (24)$$

In this simplified model it is assumed that all oxidation and gasification reactions are solid/gas type, where the solid phase is represented by the particles of inert material or coke particles when carbon take place into occurring of these reactions.

The equations which define the kinetics of combustion and gasification reactions, are carried out on the base of following expressions [6]:

For the general reaction with two reactants and two products:



the reaction rate can be expressed as follows:

$$-v = \frac{k_a}{P_x^{e+f-1}} \cdot \frac{\left[ x_E^e \cdot x_F^f - \left( \frac{x_G^g \cdot x_H^h}{P_x^{g+h-e-f} \cdot K_{eq}} \right) \right]}{\sum \left( \frac{1}{p + K_{a,i}} \right) \cdot x_i} \cdot \left( \frac{x_{9,0}}{x_9} \right)^{\frac{1}{3}} \cdot \frac{x_9}{\rho_c \cdot d_{c,0}} \quad (26)$$

if the solid phase is represent by the char particles, and by the expression:

$$-v = \frac{k_a}{P_x^{e+f-1}} \cdot \frac{\left[ x_E^e \cdot x_F^f - \left( \frac{x_G^g \cdot x_H^h}{P_x^{g+h-e-f} \cdot K_{eq}} \right) \right]}{\sum \left( \frac{1}{p + K_{a,i}} \right) \cdot x_i} \quad (27)$$

Where:

$$P_x = \frac{1}{p} \sum x_i = \frac{x_i}{p_i} \quad (28)$$

On the fluidized bed surface, all gases - products of successive reactions of pyrolysis, combustion and gasification are present, plus char solid particles, which did not react into the fluidized bed.

The molar rates of all gas components on the fluidized bed exit are determined with usage of presented gasification model.

## CONCLUSION

The global combustion and gasification processes, modeled by theoretical model, involve all the cited steps and the kinetic reactions. In addition, the operating temperature should be considered as a main factor that governs the importance of each step.

The reactors for biomass and solid waste gasification are generally constrained to the range 700-900°C. Because of the fact that in this temperature range, diffusion effects are not the limiting factor, only adsorption, surface reaction, and de-sorption on the pore walls and/or on the external surface, are taken into account.

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