

# Mathematical model of pollutants emission from biomass and sewage sludge co-combustion process

JAN NADZIAKIEWICZ, RAFAL CZEKALSKI  
 Department of Technology and Equipment for Waste Management  
 Silesian University of Technology  
 Konarskiego 18, 44-100 Gliwice  
 POLAND

*Abstract:* The paper presets model of combustion of solid waste substances in fixed bed and its application in case of co-combustion process of mixture of wood chips and sewage sludge. The model consists of mass and energy balances of gas and solid fractions. The main aim of the calculation presented in the paper is investigation of influence of sludge part in the mixture on process run and emission of gaseous hazardous substances, like hydrocarbons, sulphur oxides, nitrogen oxide and hydrogen chloride.

*Key-Words:* co-combustion, biomass, sludge, pollutants, emission, model

## 1 Introduction

As a result of EU policy, which impose an increase of use of renewable sources in energy production, biomass becomes important source of energy. Table 1 presents the amount of energy produced from waste and biomass combustion in EU and Poland. In EU the meaning of biomass in production of renewable energy has grown over the last years, in Poland it has started in the last 6 years.

**Table 1** Production of renewable energy from biomass and waste in thousands of toe. (1 toe = 41,868 GJ)

	1995	2000	2004
EU	49879	58246	71547
Poland	3762	3625	4126

In 2005, in Poland, over 2% of total produced energy was generated in boilers fed with biomass and firewood, and this amount in future will grow, according to National Strategy of Waste Management. Theoretical investigation of biomass combustion process is very important from viewpoint of its future application in practice with high efficiency and low harmful impact on the environment.

## 2 Aims and assumptions of the model

The main aim of the model is an analysis of influence of sewage sludge mass fraction in biomass-sewage mixture on total emission of harmful gaseous substances as well as on the process run. The model focuses on changes taking place in segment of fixed bed which travels through combustion chamber on mechanical stoker. The model assumptions are:

- solid fraction consists of moisture, volatile matter, carbon and ash,
- the particles are considered as spheres, but the ratio of area to volume is one of the model parameter,
- products of devolatilization process depend on temperature and heating rate,
- char combustion depends on particle surface area,
- considered gaseous pollutants are: CO, hydrocarbons, NO, SO<sub>x</sub>, HCl,
- pressure along the bed is constant, and equal to ambient pressure.

## 3 Mathematical description of the process

Four processes are considered in the model: drying, devolatilization, char combustion and reactions in gaseous phase.

### 3.1 Drying

The drying rate proceeds on particles' surface and depends on temperature and mass transfer coefficient  $\beta$  [1]. The source of H<sub>2</sub>O is defined by eq. 1:

$$S_{H_2O} = a \cdot \frac{\beta \cdot (p_{sH_2O} - p_{H_2O}) \cdot 1000}{R_{H_2O} \cdot T} \quad (1)$$

### 3.2 Devolatilization

Devolatilization process is modelled as a first order reaction. Arrhenius formula gives process rate  $k_{vol}$  (eq. 2):

$$k_{vol} = A_{vol} \cdot \exp \frac{-E_{vol}}{R \cdot T} \quad (2)$$

The parameter are: constant  $A_{vol,b} = 1.2 \cdot 10^9$  1/s and activation energy  $E_{vol,b} = 121.4$  kJ/mol for biomass (wood chips) [2] and  $A_{vol,s} = 3 \cdot 10^{15}$  1/s and  $E_{vol,s} = 275$  kJ/mol for sewage sludge [12].

The amount of volatile matter  $c$  at the end of time step  $\Delta\tau$  is:

$$c = c_0 \cdot \exp(-k_{vol} \cdot \Delta\tau) \quad (3)$$

The source of volatile matter  $S_{vol}$  is:

$$S_{vol} = \frac{c_0 - c}{\Delta\tau} \quad (4)$$

In Eq. 3 and 4  $c_0$  is amount of volatile matter at the beginning of time step. The products of devolatilization process are:  $CO_2$ ,  $CO$ ,  $H_2$ ,  $CH_4$ ,  $C_xH_y$  and tar. In case of biomass, mass fraction of tar in volatile matter is a function of heating rate [3,4,5], and composition of gaseous products depends on temperature (Fig. 1). Suitable functions for calculating composition of gaseous products were obtained on the basis of numerous investigations [3,4,5,6]. In case of sludge, composition of volatile matter depends on temperature only (Fig. 2) [12].

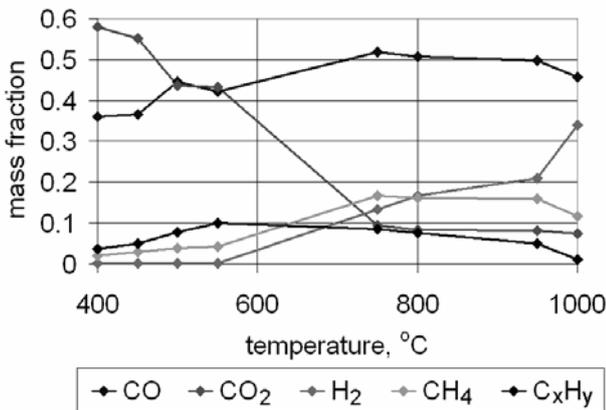


Fig. 1 Composition of gaseous products of biomass devolatilization process [4,5,6].

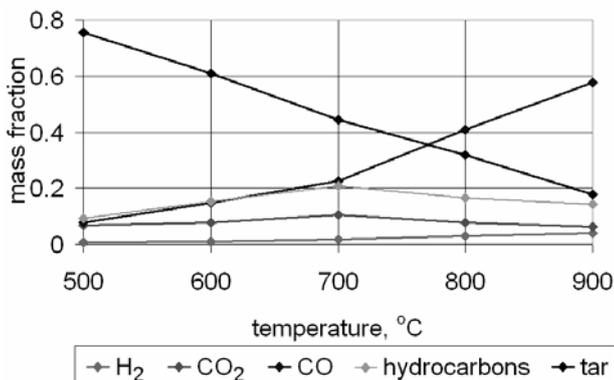
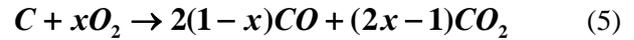


Fig. 2 Composition of volatile products of sewage sludge devolatilization process [12].

### 3.3 Char combustion

Char combustion proceeds on particles' surface. The process is limited by oxygen diffusion to the surface (at high temperatures) and by kinetics of the process (at low temperatures) [6, 7]. Products of char combustion are  $CO$  and  $CO_2$ , according to the reaction 5:



Stoichiometric factor  $x$  in this reaction represents  $CO/CO_2$  ratio (eq. 6), which is a function of temperature (eq. 7) [6]:

$$x = \frac{2 + \frac{CO}{CO_2}}{2 \cdot \frac{CO}{CO_2} + 2} \quad (6)$$

$$\frac{CO}{CO_2} = 2500 \cdot \exp\left(-\frac{6240}{T}\right) \quad (7)$$

The source of gaseous products from char combustion process is:

$$S_{char} = a \cdot p_{O_2} \cdot \left( \frac{1}{k_d} + \frac{1}{k_{ch}} \right)^{-1} \quad (8)$$

### 3.4 Reactions in gaseous phase

As the solid substance is heated up, the devolatilization products evolves to the gas phase. In gas phase a combustion process proceeds, which is a source of thermal energy. In the model, 16 homogenous reactions in gas phase are considered (Tab. 2). Tab. 2 contains also reference literature, where kinetic data of reaction are presented. Reaction rate depends on gas temperature and mixing rate of substrate with oxygen. The final reaction rate, which is a source of substances in mass balance equations, is lower value of the one calculated from kinetic parameters and mixing rate calculated as follows [10]:

$$S_{mix} = 0.65 \rho_g \cdot \left( 150 \frac{D \cdot (1-\varepsilon)^{\frac{2}{3}}}{d_p^2 \cdot \varepsilon} + 1.75 \frac{w \cdot (1-\varepsilon)^{\frac{1}{3}}}{d_p \cdot \varepsilon} \right) \cdot \text{MIN} \left\{ \frac{g_i}{F_i}, \frac{g_{O_2}}{F_{O_2}} \right\} \quad (9)$$

### 3.5 General form of model equation

The presented model consists of mass and energy balance equations. The general form of used equation is:

$$\frac{\partial(\rho \cdot \Phi)}{\partial t} + \frac{\partial(\rho \cdot w \cdot \Phi)}{\partial x} = \frac{\partial}{\partial x} \left( \Gamma \cdot \frac{\partial \Phi}{\partial x} \right) + S \quad (10)$$

The equation consists of unsteady term, convection term (does not exist in energy balance of solid phase), diffusion term (does not exist in gas continuity equation) and source term. The meaning of dependent variable  $\Phi$ ,

diffusion coefficient  $\Gamma$  and source  $S$  in individual equations are given in Tab. 3.

**Tab. 2** Reactions applied in the model and reference literature with kinetic data.

Reaction	Ref.
$CO + 0.5O_2 = CO_2$	[8]
$CH_4 + 1.5O_2 = CO + 2H_2O$	[9]
$H_2 + 0.5O_2 = H_2O$	[10]
$C_xH_y + (0.5x+0.25y)O_2 = xCO + 0.5yH_2O$	[9]
$CH_{1.84}O_{0.96} + 0.48O_2 = CO + 0.92H_2O$	[9]
$HCN + 0.5O_2 = CNO$	[13]
$CNO + 0.5O_2 = NO + CO$	[13]
$CNO + NO = N_2O + CO$	[13]
$NH_3 + 0.75O_2 = 0.5N_2 + 1.5H_2O$	[13]
$NH_3 + 1.25O_2 = NO + 1.5H_2O$	[13]
$NO + CO = 0.5N_2 + CO_2$	[13]
$H_2S + 0.5O_2 = SO + H_2$	[14]
$SO + O_2 = SO_2 + 0.5O_2$	[14]
$SO_2 + 0.5O_2 = SO_3$	[14]
$SO_3 + 0.5O_2 = SO_2 + O_2$	[14]
$SO_3 + SO = 2SO_2$	[14]

**Tab. 3** Variables in model equations.

Equation	Dependent variable $\Phi$	Diffusion coefficient $\Gamma$	Source $S$
Energy balance of solid fraction	Solid phase temperature: $T_s$ , K	Heat conduction coefficient: $\lambda_s$ , W/m·K	<ul style="list-style-type: none"> <li>convective gas-solid heat source, <math>Q_{g-s}</math></li> <li>heat of moisture evaporation, <math>Q_{H_2O}</math></li> <li>heat of char combustion, <math>Q_s</math></li> </ul>
Energy balance of gas fraction	Gas phase enthalpy: $i_g$ , J/kg	Ratio of gas conduction coefficient $\lambda_g$ to gas heat capacity $c_g$ , kg/(m·s)	<ul style="list-style-type: none"> <li>convective solid-gas heat source, <math>Q_{s-g}</math></li> <li>heat of gas reaction, <math>Q_g</math></li> </ul>
Mass balance	Mass fraction: $g_i$	Dynamical diffusion coefficient $\delta_{i-gas}$ , kg/(m·s)	Mass source of $i$ substance $S_i$ , kg/(m <sup>3</sup> ·s)
Gas cont.	Gas velocity: $w$		<ul style="list-style-type: none"> <li>moisture source, <math>S_{H_2O}</math></li> <li>devolatilization products source, <math>S_{vol}</math></li> <li>char combustion source, <math>S_s</math></li> </ul>

Set of equations is solved by discretization method described in [11]. Initial conditions are defined gas stream, as well as gas and solid temperature. Boundary

conditions are temperature and heat transfer coefficient over the bed.

**Tab. 4** Initial and boundary conditions used in calculation.

Bed height, m	0.1
Bed diameter, m	0.15
Temperature over the bed, K	1273
Air parameters	
Stream, kg/m <sup>2</sup> ·s	0.36
Temperature, K	293
Nitrogen (molar fraction)	0.79
Oxygen (molar fraction)	0.21
Humidity	0.4

**Tab. 5** Wood and sludge properties.

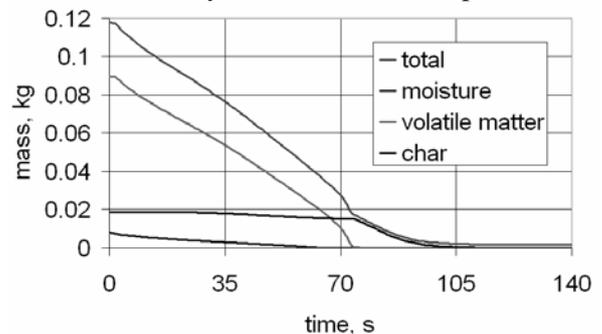
	Proximate analysis			
	moisture	volatile matter	char	ash
wood	0.05	0.78	0.164	0.006
sludge	0.45	0.32	0.05	0.18
	Ultimate analysis			
	sulphur	nitrogen	chlorine	
wood	$1.9 \cdot 10^{-4}$	$1.22 \cdot 10^{-3}$	$1.22 \cdot 10^{-4}$	
sludge	$5.9 \cdot 10^{-3}$	$4 \cdot 10^{-2}$	$5 \cdot 10^{-4}$	

### 4 Results of calculations

This section presents results of modelling of co-combustion process of wood chips and sewage sludge mixture in fixed bed. Tab. 4 contains initial and boundary conditions. The boundary conditions are temperature over the bed and heat transfer coefficient. Tab. 5 presents wood and sludge properties.

Figures 3 and 4 present results of calculation of one example case, where sludge mass fraction is 5%.

Mass loss history of the bed and its main components is presented on Fig. 3. The whole process lasts about 110 s, while moisture evaporates before 70 s and just after this period, the volatile matter is also released. From this moment on, only carbon combustion proceeds.



**Fig. 3** Mass loss history of the bed during wood chips and sludge co-combustion process.

Figure 4a presents mass fraction of  $O_2$ ,  $CO$ ,  $CO_2$ ,  $H_2O$  and tar in gas at the top of the computation domain (height 0.1 m) in time. Three essential periods of the process are seen. The first one, is initial heating up and drying. This period lasts about 10 s, and it is connected with abrupt grow of moisture, and devolatilization products in gas phase. As the time passes, the devolatilization products (here represented by tar) react with oxygen, and after 10 s the second period begins. This one is dominated by drying and devolatilization processes and combustion of gaseous products in gas phase. The amount of  $O_2$  slowly decreases, while products of combustion  $CO$  and  $CO_2$  increases. The third period starts at about 80 s. From this moment on, there is no more volatile matter in the bed, and in this period only carbon burn-out process proceeds. Now, the amount of oxygen in gas is enough to burn the char completely, and this reaction proceeds till the end of whole process. Because of high temperature, the main product of this heterogeneous reaction is  $CO$  (according to Eq. 5).

Figure 4b presents content of  $H_2$ ,  $CH_4$ , and  $C_xH_y$  in gaseous phase at the height of 0.1 m. Those devolatilization products also do not react completely, though there is oxygen in gas. Kinetics and mixing rate of gases plays important role in reactions' run. During the second period of the process (the one dominated by drying and devolatilization), their levels in gas are much about constant. Their amounts are higher at the beginning and at the end, because in these periods the layer of bed with high temperature is higher than during the period of domination of devolatilization process.

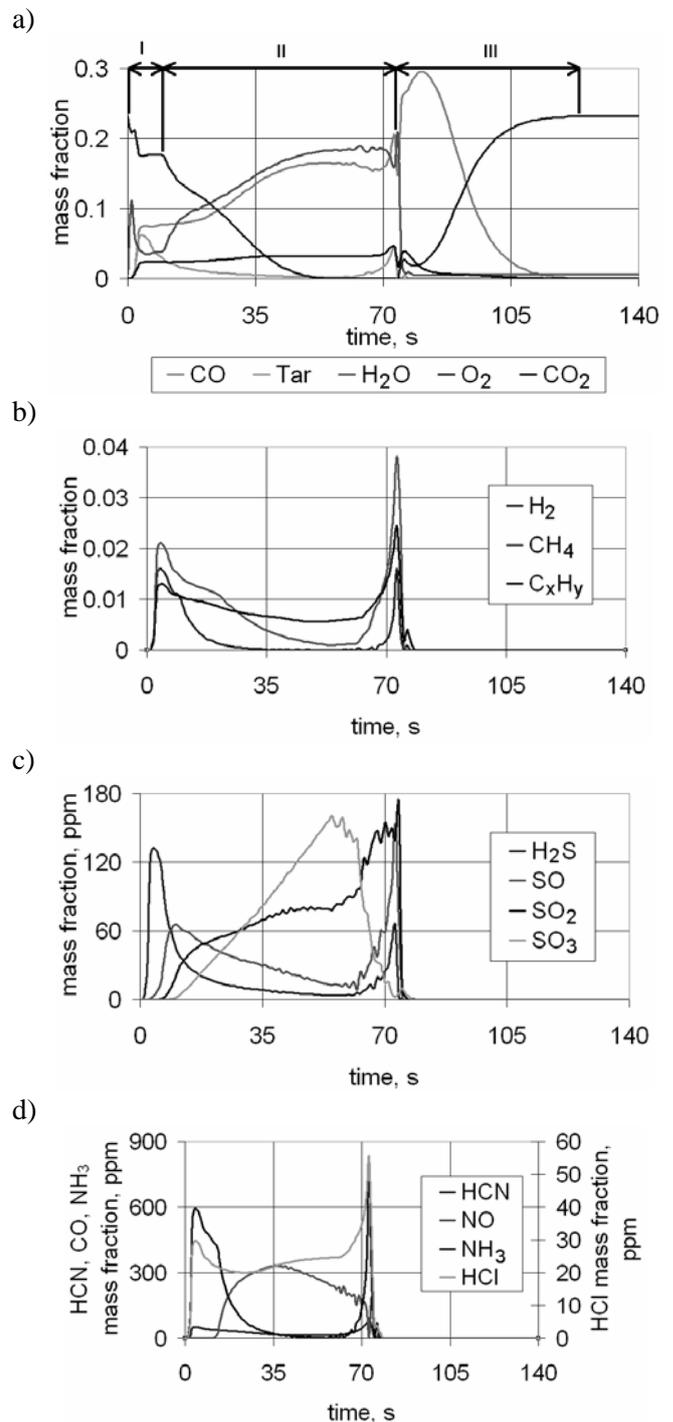
Sulfur oxides and hydrogen sulfide mass fractions over the bed are presented on Fig. 4c.

The source of  $SO_x$  in gas is  $H_2S$  which evolves from solid fraction during heating up. At the beginning of the process, when gas temperature is low,  $H_2S$  is the main compound containing sulfur in gas. As the gas temperature grows,  $H_2S$  begins to oxidize to  $SO$ , and then completely oxidation of  $SO$  to  $SO_3$  proceeds. At the end of the second period, when gas temperature decreases,  $SO_2$  dominates in gas.

Nitrogen compounds and hydrogen chloride mass fractions in gas are presented on Fig. 4d. The source of nitrogen compounds in gas are  $NH_3$  and  $HCN$ , which evolve from solid fraction in devolatilization process. As the gas temperature grows, the majority of those substances oxidizes to  $NO$ , which is the main compound of nitrogen in gas phase during the better part of the process. After 40 s  $NO$  level decreases as a result of its reduction to  $N_2$ .  $HCl$  in gaseous phase comes from devolatilization process and is a function of chlorine content in solid fraction.

Having the code, one can calculate the influence of sludge mass fraction in the fuel mixture on the

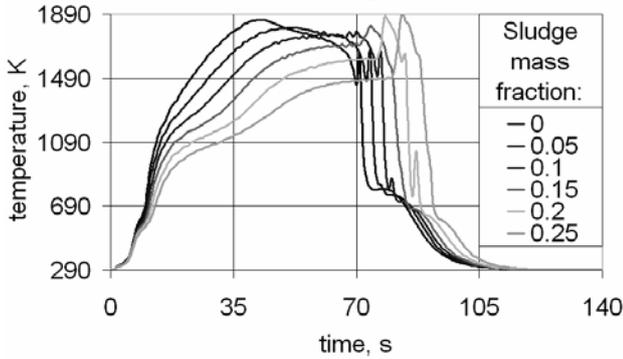
parameters of the process. The higher content of sludge in fuel mixture, the higher moisture content, which has influence on process condition.



**Fig. 4** Gas composition at height 0.1 m over the bed.

Gas temperature, which has significant influence on reactions in gaseous phase, becomes lower and second period of the process becomes longer. The last peak is connected with char combustion. Gas temperature above the bed is presented on Fig. 5.

Figure 6 presents total emission of gaseous substances related to initial mass of solid fraction. The emission is related to the initial total mass of solid fraction. Sources of CO and CO<sub>2</sub> in gaseous products are char and volatile matter. As the amount of sludge grows in mixture, char and volatile matter content decrease which affects also total emission of CO<sub>2</sub> and CO (Fig. 6a).



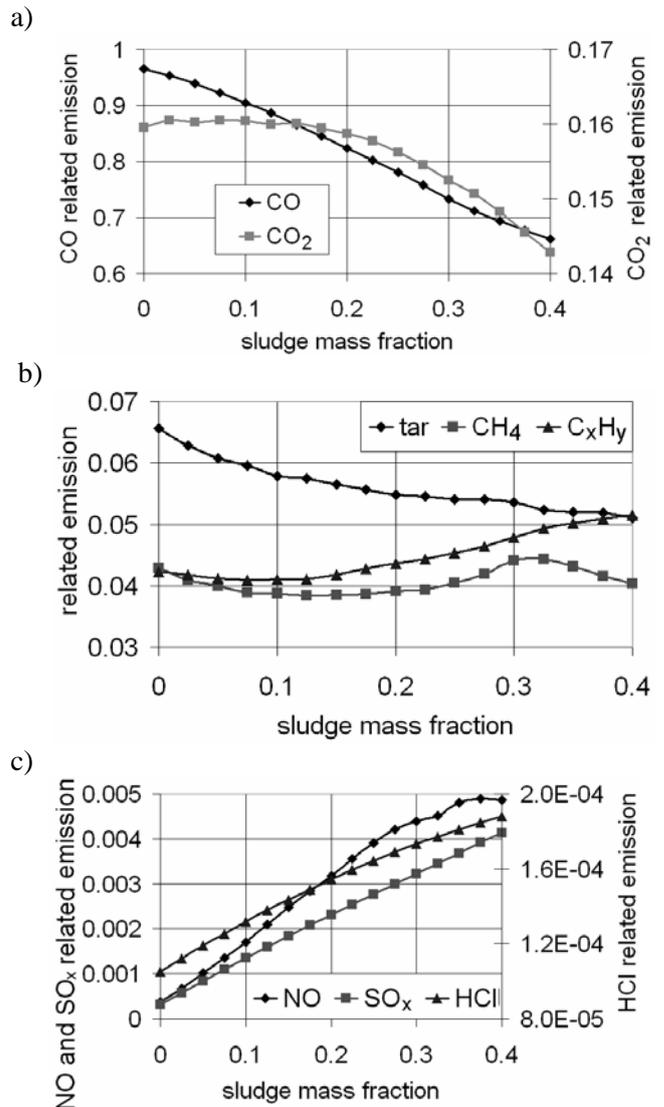
**Fig. 5** Gas temperature over the bed for different wood chips and sludge mixtures.

Volatile matter in solid fraction are source of hydrocarbons in gaseous phase. The amount of hydrocarbons depends indirectly on mixture composition. Fuel mixture has an influence on process conditions, like temperature and process rate, which determine composition of evolving volatile matter according to the functions presented on Fig. 1, 2 and 3. Fig. 6b presents total emission of hydrocarbons. Because tar is the major product of devolatilization process, in case of wood as well as sludge, its emission decreases with increase of sludge mass fraction (which lessens the volatile matter in mixture). Higher hydrocarbons C<sub>x</sub>H<sub>y</sub> has an opposite tendency. In case of these substances, gas temperature has a greater influence on the emission. The lower temperature, the lower efficiency of C<sub>x</sub>H<sub>y</sub> combustion. In case of methane, those two factors has an influence on its emission which has changeable tendency in investigated range of sludge mass fraction in mixture.

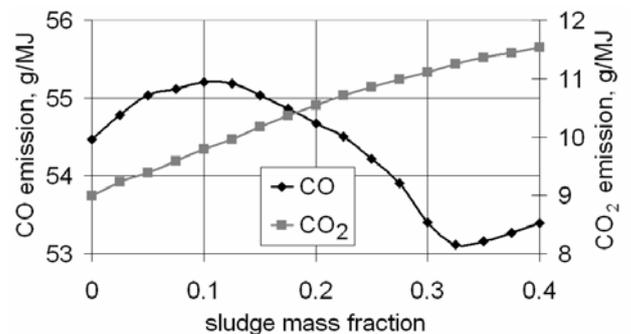
The growth of sludge in mixture increases content of sulphur, nitrogen and chlorine in total mass of mixture. This is the reason of higher emission of SO<sub>x</sub>, NO and HCl. As it is seen on Fig. 6c, emission of those substances depends directly on content of S, N and Cl in sample, and process parameters have no important influence on its emission.

With the growth of sludge mass fraction in mixture, its calorific value, as well as the amount of energy generated in the process, decreases. Total emission of gaseous substances, related to MJ of chemical energy contained in mixture increases in case of all substances with the growth of sludge mass fraction in mixture. The exception is emission of CO, which decreases in range 10-32% of sludge in mixture, and for mixtures

containing amount of sludge over 32%, CO emission grows (Fig. 7).



**Fig. 6** Emissions of gaseous substances related to initial mass of solid fraction as a function of sludge mass fraction



**Fig. 7** Emissions of CO and CO<sub>2</sub> substances related to chemical energy contained in solid fraction as a function of sludge mass fraction

## 5 Conclusion

The paper presents model of biomass combustion process in fixed bed. A two dimensional steady process of moving bed along combustion chamber (which is simplification of real 3D process) was substituted by one dimensional unsteady process of combustion of bed segment. The state of segment in time steps corresponds to different position of segment on the grate. The aim of the model was calculation of total emission of hazardous substances in mixture of wood chips and sludge in different proportions.

The whole process may be divided in three characteristic periods: the first one is the shortest one, and is caused by high temperature over the bed, which initiates the whole process. In this period, an abrupt changes of gas amount and composition occurs. As the time pass, the process stabilizes and the second period begins. In this period drying and devolatilization processes of solid fraction proceeds as well as combustion reactions in gaseous phase. Reactions are determined by kinetic parameters and mixing rate of substrates, thus not all hydrocarbons burns completely. Gas composition and temperature in this period generates nitrogen and sulphur oxides.

Mixture composition has an influence on parameters and run of the process. These parameters (heating rate of solid fraction and gas temperature) determine products of devolatilization process and efficiency of reaction in gaseous phase. Emission of CO, CO<sub>2</sub> as well as NO, SO<sub>x</sub> and HCl depends generally on composition of solid fraction. In case of CO and CO<sub>2</sub>, emission decreases with the growth of sludge content in mixture, on the other hand, emission of NO, SO<sub>x</sub> and HCl increases. Hydrocarbons emission depends indirectly on mixture composition. Mixture composition determines process parameters, which has direct influence on emission of hydrocarbons.

This model may also predict influence of other factors on total emission, like moisture content, air stream, initial and boundary conditions. Application of developed models of reactions in gaseous phase may give more precise information about emission of hazardous substances.

## Acknowledgment

This work is financed by Ministry of Science and Higher Education in Poland, as an research project in years 2006-2007.

## Nomenclature

$S$  – mass source, kg/ m<sup>3</sup>·s  
 $a$  – volumetric area, m<sup>2</sup>/m<sup>3</sup>  
 $\beta$  – mass transfer coefficient, m/s  
 $p_{sH_2O}$  – saturation pressure of H<sub>2</sub>O, kPa  
 $p$  – partial pressure, kPa

$R_{H_2O}$  – gas constant of H<sub>2</sub>O, J/kg·K  
 $T$  – temperature, K  
 $A$  – Arrhenius constant, 1/s  
 $E$  – activation energy, kJ/mol  
 $R$  – universal gas constant, kJ/mol·K  
 $c$  – mass concentration, kg/m<sup>3</sup>  
 $\Delta\tau$  – time step, s  
 $k$  – process rate, kg/m<sup>2</sup>·s·kPa  
 $\rho$  – density, kg/m<sup>3</sup>  
 $D$  – kinematical diffusion coefficient, m<sup>2</sup>/s  
 $\epsilon$  – bed porosity  
 $d_p$  – particle diameter, m  
 $w$  – gas velocity, m/s  
 $g$  – mass fraction  
 $F$  – stoichiometric factor in reaction  
 $Q$  – heat of reaction, W/m<sup>3</sup>  
 $\lambda$  – heat conduction coefficient, W/m·K  
 $i$  – enthalpy, J/kg  
 $c$  – heat capacity, J/kg·K  
 $\delta$  – dynamical diffusion coefficient, kg/m·s

## Subscripts

$H_2O$  – moisture  
 $O_2$  – oxygen  
 $vol$  – volatile matter  
 $d$  – diffusion  
 $ch$  – chemical reaction  
 $s$  – solid  
 $g$  – gas  
 $i$  – gas component

## References:

- [1] Wakao N., Kagueli S.: *Heat and mass transfer in packed bed*, Gordon and Breach Science Publishers, New York 1982
- [2] Senneca O., *Fuel Proc. Techn.* 88 (2007) 87–97
- [3] Ramadesh R. et al., *Fuel* 85 (2006) 1211-1220
- [4] Horne P.A, Williams P.T, *Fuel* 75 (1996) 1051-1059
- [5] Zanzi R. et. al., *Biomass Bioen.* 23 (2002) 357 – 366
- [6] Douglas Smoot L., Smith P.J.: *Coal Combustion and Gasification*, Plenum Press, New York 1985
- [7] Nadziakiewicz J.: *Spalanie stałych substancji odpadowych*, Wydawnictwo Gnome, Katowice 2001
- [8] Shin D,Choi S, *Combust. Flame* 121 (2000) 167-180
- [9] Zhou H. et al., *Fuel* 84 (2005) 389-403
- [10] Yang Y.B. et al., *AIChE J.* 52 (2006), 809-817
- [11] Patankar S.V.: *Numerical Heat Transfer and Fluid Flow*, Hemisphere Publishing Corporation 1980
- [12] Werther J., Ogada T., *Prog. Energy Combust. Sci.* 25 (1999) 55-116
- [13] Desroches-Ducarne E.: *Fuel* 77 (1998) 1399-1410
- [14] Cerru F.G et. al., *Combust. Flame* 146 (2006) 437-455