The 8ᵗʰ International Conference on Applied Energy – ICAE2016

A Model for the Prediction of Pollutant Species Production in the Biomass Gasification Process

Agostino Gambarotta, Mirko Morini*, Andrea Zubani

Industrial Engineering Department, University of Parma, Parco Area delle Scienze 181/a, 43125 Parma, Italy

Abstract

This paper presents a non-stoichiometric equilibrium model for the simulation of biomass downdraft gasifiers. The chemical equilibrium is determined by minimizing the Gibbs free energy. Five elements characterize the biomass and 15 chemical species are considered in the syngas. The model calculates the lower heating value of the syngas and the relative abundances of gasification products. An advantage of this model is that it can easily calculate not only the concentrations of the main gasification products, but also the concentrations of minor product, especially the pollutant chemical species containing Nitrogen and Sulfur.

To analyse the model behaviour, a sensitivity analysis on process parameters is presented. The model is validated by comparing its results with the results of simulation carried out with a stoichiometric model and with experimental data found in literature. Finally, the model is applied to the study of the gasification of forest waste.

Keywords: biomass, gasification, pollutant, energy.

1. Introduction

Biomass gasification is one of the most promising technology for energy exploitation of products, by-products and residues from agriculture, forestry and livestock farming. The main advantage of gasification is that using a gaseous fuel (i.e. the syngas, which is the product of biomass gasification) is potentially more efficient than direct combustion of solid biomass, because syngas can be burned at higher temperatures.

───────

* Corresponding author. Tel.: +39 0521 905714.
E-mail address: mirko.morini@unipr.it.

To simulate the biomass gasification process, three different approaches has been used in literature: CFD modeling, kinetic modeling and equilibrium modeling.

CFD models [1] can simulate a wide range of physical phenomena, but they need a high amount of computational resources.

Kinetic modeling [2] can produce accurate results, but also this kind of model is quite complex. An advantage of these models is that they can be suitable for studies on the influence of reactor design and process parameters (reaction rate, residence time, etc.).

Equilibrium models [3,4] are simple and fast. Practically, equilibrium condition is never reached within the gasifier, nevertheless these models can describe gasification processes with good approximation. Equilibrium models can be divided into two categories, according to the method used to calculate the chemical equilibrium: stoichiometric models and non-stoichiometric models. In stoichiometric models [4], equilibrium is determined by using the equilibrium constants for the reactions involved in the process, whereas in non-stoichiometric models [3] it is determined by minimization of the Gibbs free energy.

In this paper, a non-stoichiometric equilibrium model has been developed to simulate the behavior of a downdraft gasifier. This kind of gasifier usually operates close to equilibrium conditions, so an equilibrium approach is particularly suitable. The aim of this model it to calculate not only the concentrations of the main gasification products (CO, H_2, CH_4, CO_2, H_2O), but also the concentrations of minor products, especially the pollutant chemical species containing Nitrogen and Sulfur (e.g. NH_3, H_2S). The presence of these species is not relevant in the calculation of the heating value, but it is important because it may require the installation of systems to remove these pollutants from the syngas or in the flue gas after syngas combustion. The stoichiometric approach needs a detailed specification of all the chemical reactions that occur in the reactor. When many chemical species are involved, it can be very difficult to foresee which reactions will take place in the reactor. For this reason, a non-stoichiometric approach has been used in the present work.
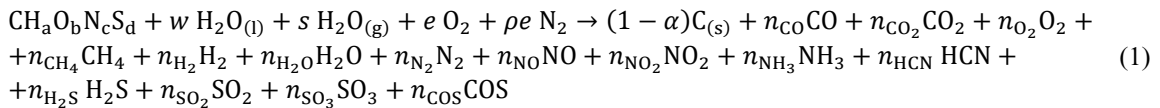

Nomenclature

w	moisture of biomass [mol]
s	steam [mol]
e	oxygen [mol]
ρ	nitrogen to oxygen molar ratio in oxidant
α	fraction of carbon atoms participating in equilibrium reaction
n	number of moles
G	total Gibbs free energy [J]
G°	standard Gibbs free energy [J/mol]
R	universal gas constant [J/(mol*K)]
T	process temperature [K]
T_{in}	reagents temperature [K]
L	Lagrangian function

λ	Lagrange multiplier
m	number of atoms in chemical species
M	number of atoms in the reagents
H°	standard enthalpy of formation [J/mol]
c_p	specific heat at constant pressure [J/(mol*K)]
Q_{loss}	heat lost through reactor's wall [J/mol biomass]

2. Model development and implementation

To simplify the problem, only chemical species containing C, H, O, N and S are considered in this model. A total of 16 products is considered. All of gasification products are supposed to be in gaseous phase, except for unconverted solid carbon C(s). The global reaction inside the gasifier can be described as follows:

$$CH_aO_bN_cS_d + w\,H_2O_{(l)} + s\,H_2O_{(g)} + e\,O_2 + \rho e\,N_2 \rightarrow (1-\alpha)C_{(s)} + n_{CO}CO + n_{CO_2}CO_2 + n_{O_2}O_2 +$$
$$+n_{CH_4}CH_4 + n_{H_2}H_2 + n_{H_2O}H_2O + n_{N_2}N_2 + n_{NO}NO + n_{NO_2}NO_2 + n_{NH_3}NH_3 + n_{HCN}\,HCN + \quad (1)$$
$$+n_{H_2S}\,H_2S + n_{SO_2}SO_2 + n_{SO_3}SO_3 + n_{COS}COS$$

where n_i is the number of moles of the *i*-th chemical species, ρ is the Nitrogen to Oxygen molar ratio in the oxidant (e.g. 3.76 for standard air) and α is a factor introduced in order to consider that not all the carbon participate to the process. This factor is a function of the air-to-fuel ratio and can be calculated using empirical correlations [5]. All gaseous chemical species are considered as ideal gases. The production of tar is neglected, as usually done in literature when dealing with equilibrium models of downdraft reactors [3,4,5]: in fact, in these kind of reactors the amount of tar which leaves the gasifier is minimal. All reagents are supposed to enter into the reactor at temperature T_{in}, and all products are supposed to leave the reactor at the process temperature T. The process temperature is assumed to be constant inside the gasifier, this is a common assumption in equilibrium models [3,4,5].

At the equilibrium state, the total Gibbs free energy of a gas mixture composed by M chemical species can be represented by:

$$G = \sum_{i=1}^{M} n_i G_i^{\circ} + \sum_{i=1}^{M} n_i RT \cdot ln(n_i/n_{tot}) \quad (2)$$

where G_i° is the standard Gibbs free energy of the *i*-th species, R is the universal gas constant and T is the temperature. To calculate the composition of syngas, it is necessary to find the values of n_i which minimize the objective function G. This optimization problem has two families of constraints: the mass balance between reagents and products and the non-negativity of the numbers of moles n_i.

To solve this optimization problem, the method of Lagrange multipliers is used. For every mass balance constraint, a Lagrange multiplier λ_k is introduced. In this model, five elements are considered, so five Lagrange multipliers are introduced ($\lambda_C, \lambda_H, \lambda_O, \lambda_N, \lambda_S$). The Lagrangian function L can be written as:

$$L = G - \sum_{k=1}^{5} \lambda_k \left(m_{i,k} n_i - M_k \right) \quad (3)$$

where $m_{i,k}$ is the number of atoms of k-th element in a molecule of the i-th chemical species, and M_k is the number of atoms of the k-th element in the reagents. This function is minimized when all its partial derivatives are equal to zero:

$$\left(\frac{\partial L}{\partial n_i}\right) = 0 \quad ; \quad \left(\frac{\partial L}{\partial \lambda_k}\right) = 0 \tag{4}$$

These conditions can be written as a system of non-linear equation. This system can be solved by using an iterative method. In the present work, the RAND method is used [6].

To calculate the reaction temperature, the energy balance equation is used:

$$\sum_{j=1}^{N} n_j \left(H_{f,j}^{\circ} + \int_{T_{rif}}^{T} c_{p,j} \, dT\right) = \sum_{i=1}^{M} n_i \left(H_{f,i}^{\circ} + \int_{T_{rif}}^{T} c_{p,i} \, dT\right) + Q_{loss} \tag{5}$$

where N is the number of reagents, H_f° and c_p are respectively the standard enthalpy of formation and the specific heat at constant pressure of the i-th or j-th chemical species, Q_{loss} is the heat lost through reactor's wall referred to one mole of biomass.

To calculate the reaction temperature, a first iteration value is assumed, and used to calculate the composition of syngas. These values of temperature and composition are substituted in the energy balance equation (Eq. 5). In particular, this model calculates the unbalance ΔH of Eq. 5 and adjusts the temperature until ΔH approaches zero. A scheme of this procedure is shown in Fig. 1.
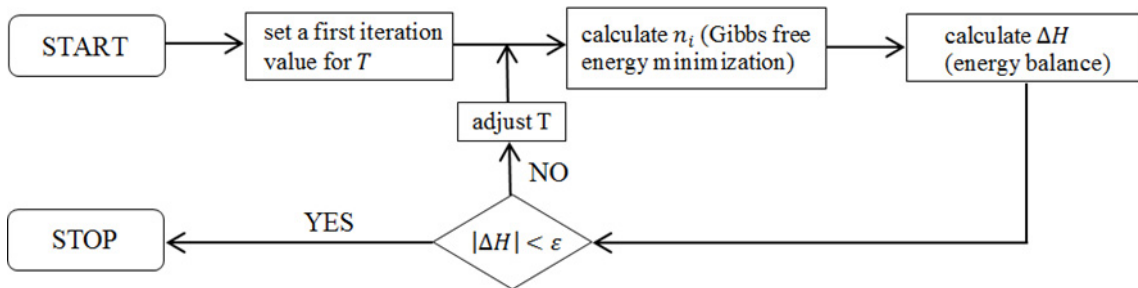

Fig. 1. Flow chart for the calculation procedure

3. Results and discussion

A sensitivity analysis has been performed by varying air-to-fuel ratio and biomass humidity. In particular, syngas composition and its lower heating value are evaluated. For the sake of readability only the main species are reported. Fig. 2a shows the results of the sensitivity analysis for the air-to-fuel ratio (in abscissa process temperature which is a result of the simulation, i.e. increases by increasing the air-to-fuel ratio, is reported). It can be noticed that the lower heating value decreases by increasing process temperature. This is due to the fact that, in order to reach high temperatures, the combustion process need to proceed further. When temperature increases, the volume fractions of CO and N_2 increase, whereas the fractions of CO_2, CH_4 and H_2 decrease. The volume fraction of water decreases until about 1000 K, then it increases. Fig. 2b shows the results of the sensitivity analysis for biomass humidity. An increase in biomass humidity causes a decrease of the lower heating value, this is due to the fact that a higher amount of energy is exploited for water evaporation and, therefore, it is not available in the syngas.
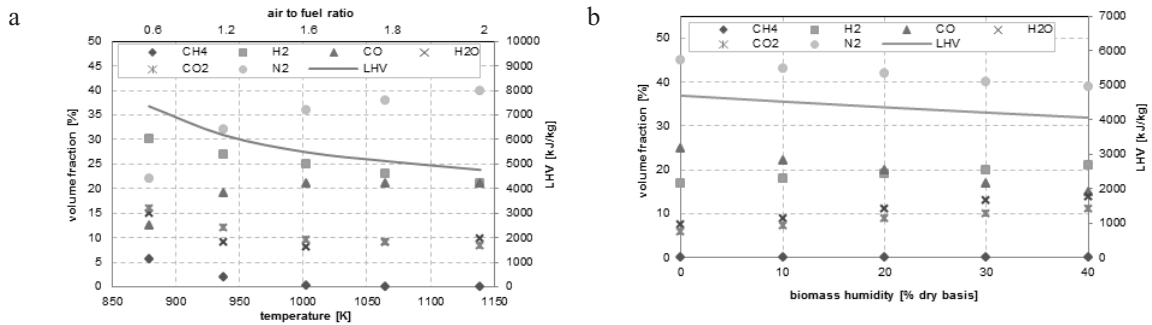
a

b

Fig. 2. (a) Air-to-fuel ratio sensitivity analysis (biomass: a=1.54, b=0.62; humidity on dry basis: 16%; oxidant: air) (b) Biomass humidity sensitivity analysis (biomass: a=1.54, b=0.62; oxidant: air; air-to-fuel ratio equal to 2.2)

The model is then validated by comparing the results with experimental data found in literature [7] and with a stoichiometric model [4]. Also in this case, the results are presented in Tab. 1 for energy related species since in literature only these data are available.

It can be noticed that the model overestimates the volume fraction of H_2 and underestimates CO and CH_4 fractions. These lead to an error equal to 18.5 % on the evaluation of the lower heating value with respect to the experimental data, but these are well-known weakness of equilibrium models and. In fact, the comparison with the stoichiometric model [4] shows similar results.

The model is then applied to forest waste gasification. This biomass is assumed to have a moisture content of 40 % and a composition characterized by a=1.4, b=0.85, c=0.02, d=0.00004.

Fig.3a shows the main products of gasification and the lower heating value of syngas for different values of the air-to-fuel ratio. An increase in the air-to-fuel ratio causes an increase in oxidized compounds and a decrease in the lower heating value. Fig.3b shows the minor products of gasification. NH_3 and H_2S concentrations are not negligible, especially for low air-to-fuel ratio values. HCN and COS are also present, but in lower concentrations. Their value increases since the air-to-fuel ratio increases.

Table 1. Model validation (a=1.44, b=0.66, biomass humidity equal to 20 %, process temperature equal to 1073 K)

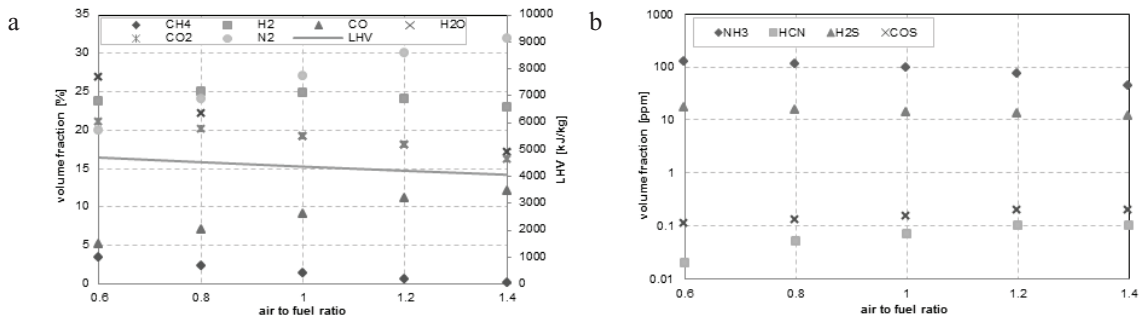| Chemical species	volume fraction (dry basis)	Current model	Model in [4]	Exp. Data in [7]
CO	[%]	21.57	20.80	23.04
H_2	[%]	25.00	23.39	15.23
CH_4	[%]	0.04	0.75	1.58
N_2	[%]	41.66	42.74	42.31
CO_2	[%]	11.73	12.31	16.42
	LHV (dry basis)	Current model	Model in [4]	Exp. Data in [7]
	[kJ/kg]	5211	5103	4398

Fig. 3. Model application to forest waste gasification (a) main products (b) minor products.

4. Conclusions

In this paper an equilibrium model for the simulation of biomass gasification has been developed and validated. The model takes into consideration five elements (C, H, O, N, S) and 16 species. The equilibrium is calculated by minimizing the syngas Gibbs free energy.

The model is validated against experimental data gathered from literature and against the results of a stoichiometric model. The model highlights the well-known weakness of equilibrium models (i.e. overestimation of H_2 and underestimation of CH_4) but proves to be effective in the simulation of biomass gasification process both for the calculation of energy related species and pollutant related species.

References

[1] Liu H, Cattolica RJ, Seiser R. CFD studies on biomass gasification in a pilot-scale dual fluidized-bed system. *International Journal of Hydrogen Energy* 2016; doi:10.1016/j.ijhydene.2016.04.205.

[2] Farid MM, Jeong HJ, Hwang J. Kinetic study on coal–biomass mixed char co-gasification with H_2O in the presence of H_2. *Fuel* 2016;**181**:1066–73.

[3] Li X, Grace JR, Watkinson AP, Lim CJ, Ergüdenler A. Equilibrium modeling of gasification: a free energy minimization approach and its application to a circulating fuidized bed coal gasifier. *Fuel* 2001;**80**:195–207.

[4] Azzone E, Morini M, Pinelli M. Development of an equilibrium model for the simulation of thermochemical gasification and application to agricultural residues. *Renewable Energy* 2012;**46**:248-54.

[5] Damiani L, Trucco A. Biomass gasification modelling: an equilibrium model, modified to reproduce the operation of actual reactors. *Proceedings of ASME Turbo Expo* 2009; **1**:493-502.

[6] Smith WR, Missen RW. *Chemical reactions and equilibrium analysis*. 2nd ed. New York: Wiley; 1982.

[7] Zainal ZA, Ali R, Lean CH, Seetharamu KN. Prediction of performance of a downdraft gasifier using equilibrium modeling for different biomass material. *Energy Conversion and Management* 2001;**42**:1499–515.

Biography

Mirko Morini received his PhD in Engineering Science in 2008 at the University of Ferrara. From 2010 to 2013 he was a researcher at the Engineering Department of the University of Ferrara and then he holds the same role at the Industrial Engineering Department at the University of Parma.