# PREDICTIONS OF THE PRODUCTS COMPOSITIONS FOR COMBUSTION OR GASIFICATION OF BIOMASS AND OTHERS HYDROCARBONS

**Hendrick Maxil Zárate Rocha, hendrick@ufpa.br**
**Yuu Itai, yuuitai@ufpa.br**
**Manoel Fernandes Martins Nogueira, mfmn@ufpa.br**
**Sinfrônio Brito Moraes, sbrito@ufpa.br**
**Brigida Ramati Pereira da Rocha, brigida@ufpa.br**

Universidade federal do Pará – Faculdade de Engenharia Mecânica, Rua Augusto Correa, no 1, 66075-900 Belém-PA

***Abstract.*** *Processes involving combustion and gasification are object of study of many researchers. To simulate these processes in a detailed way, it is necessary to solve equations for chemical kinetics whose resolution many times is difficult due lack of information in the literature a simples way to bypass tis problem is due the chemical equilibrium. Prediction of the flu gases composition through chemical equilibrium is an important step in the mathematical modelling for gasification and combustion processes. Some free programs exists to solve problems that involve the chemical equilibrium, such as STANJAN, CEA, GASEQ, CANTERA and others.These programs have difficulty for cases involving fuel such as: biomass, vegetable oils, biodiesel, natural gas, etc., because they do not have database with the fuel composition and is hard to supply their HHV and their elemtary analysis. In this work, using numeric methods, a programa was developed to predict the gases composition on equilibrium after combustion and gasification processes with the for constant pressure or vulume.*

*In the program the chemical formula of the fuel is defined as* $C_xH_yO_zN_wS_vA_u$ *that reacts with an gaseous oxidizer composed by* $O_2$, $N_2$, *Ar, He,* $CO_2$ *e* $H_2O$ *to have as final result the composition of the products* $CO_2$, *CO,* $H_2O$, $H_2$, *H, OH,* $O_2$, *O,* $N_2$, *NO,* $SO_2$, $CH_4$, *Ar, He, and ash. To verify the accuracy of the calculated values, it was compared with the program CEA (developed by NASA) and with experimental data obtained from literature.*

***Keywords***: *Combustion, Gasification, Chemical Equilibrium*

## 1. INTRODUCTION

One of the major problems especially for developing countries, is the electric power generation. Biomass fuels and residues can be converted to energy via thermal, biological and physical processes. The use of renewable natural resources as biomass and biofuels in thermal processes includes combustion and gasification to electric power generation, that has been used studied by many researchers in large-scale or small-scale. Equilibrium model has been used by many researchers for the analysis of downdraft and fluidized bed gasifiers and also in combustion and phase equilibrium problems (Gordon and MaBride, 1994). Some of those models were based on minimization of the Gibbs free energy and a another kind of equilibrium model is one based on equilibrium constants. However, the equilibrium model based on minimization of the Gibbs free energy and others based on equilibrium constants have the same basic concept, but to minimize the Gibbs free energy, constrained optimization methods are generally used which requires an understanding of complex mathematical theories. For that reason, the present work is developed based on the equilibrium constant and not on the Gibbs free energy.

Recently, many works have been published in the field of gasification and combustion modeling by chemical equilibrium and empirical relations, especially for process where the chemical formula is defined as $C_xH_yO_z$ as (Babu and Pratik, 2005) and (Zainal, 2001), but many works do not presented as final result a capable program to calculate combustion and gasification processes, where the user should only introduce the characteristics of the fuel (elementary analysis and HHV) and oxidant (air or another oxidant) in a fast and easy way. To solve this problem it was compiled a program with help of the program EES (Engineering Equations Solver) developed by (Klein and Alvarado, 2004)

## 2. METHODOLOGY

### 2.1.Equilibrium modeling

The global reaction can be written as follows:

$$\begin{aligned} C_xH_yO_zN_wS_vA_u + \propto H_2O + \beta(O_2 + aN_2 + bAr + cHe + dCO_2 + eH_2O) \\ = a_1CO_2 + a_2CO + a_3H_2O + a_4H_2 + a_5H + a_6OH + a_7O_2 \\ + a_8O + a_9N_2 + a_{10}NO + vSO_2 + a_{12}CH_4 + b\beta Ar + c\beta He + uA \end{aligned} \tag{1}$$

Where $x$, $y$, $z$, $w$, $v$ and $u$ are the number of atoms of carbon, hydrogen, oxygen, nitrogen, sulphur and ash obtained from the elementary analysis in the fuel, respectively. These coefficients are calculated as a function of the mass of dry fuel $\left(m_{f,d}\right)$ and of the mass fraction of C, H, O, N, S and Ash in the following way:

$$x = \frac{C * m_{f,d}}{100 * M_C}, y = \frac{H * m_{f,d}}{100 * M_H}, z = \frac{O * m_{f,d}}{100 * M_O}, w = \frac{N * m_{f,d}}{100 * M_N}, v = \frac{S * m_{f,d}}{100 * M_S}, u = \frac{A * m_{f,d}}{100 * M_A} \tag{2}$$

Where $M_i$ is the molecular weight of the species $i$ and $m_{f,d}$ mass of the dry fuel.

The molar quantity of water per mol of fuel ($\propto$), can be determined as a function of relative moisture of fuel (RM):

$$\propto = \frac{m_{f,s} * RM}{M_{H_2O}(100 - RM)} \tag{3}$$

All inputs on the left-hand side of Eq.(1) are defined at 25°C (298,15 K). On right-hand side, $a_i$ are the numbers of mole of the species $i$ that are also unknown.

To find the eleven unknown species of the products, eleven equations were required. Considering the global reaction in Eq.(1), the first four equations were formulated by balancing each chemical element as show in Eqs.(4)-(7).

Carbon balance:

$$x + d\beta = a_1 + a_2 + a_{12} \tag{4}$$

Hydrogen balance:

$$y + 2 \propto + 2e\beta = 2a_3 + 2a_4 + a_5 + a_6 + 4a_{12} \tag{5}$$

Oxygen balance:

$$z + \propto + \beta(2 + 2d + e) = 2a_1 + a_2 + a_3 + a_6 + 2a_7 + a_8 + a_{10} + v \tag{6}$$

Nitrogen balance:

$$w + 2a\beta = 2a_9 + a_{10} \tag{7}$$

There are four equations to find, so far, 11 variables; therefore it is necessary to add seven equations to solve the system. Notice that $v$, $b$, $c$ and $u$ are coefficients from inert species wich can be obtained direct from the reaction (1). The seven remaing equations are obtained from the equilibrium constant of the reactions involving occurring in the process, whose definition is the following:

$$K = \left[\frac{\prod_{j=1}^{m} N_j^{v_j}}{\prod_{i=1}^{n} N_i^{v_i}}\right]\left(\frac{P}{P_0 N}\right)^{\left[\sum_{j=1}^{m} v_j\right] - \left[\sum_{i=1}^{n} v_i\right]} = e^{-\frac{\sum_{j=1}^{m} \bar{G}_{T,j} - \sum_{i=1}^{n} \bar{G}_{T,i}}{R_u T}} \tag{8}$$

All gases were assumed to be ideal, no residue, absence of tar, the relationship between equilibrium constant, K, and mole of chemical species in each equation can be written as:

$$CO_2 \rightleftharpoons CO + \frac{1}{2}O_2 \qquad K_1 = \frac{a_2}{a_1}\left(\frac{P_P a_7}{P_0 N_P}\right)^{0,5} \qquad K_1 = exp\left(\left(\bar{G}_{T,CO} + 0{,}5\bar{G}_{T,O_2} - \bar{G}_{T,CO_2}\right)/R_u T\right) \tag{9}$$

$$\frac{1}{2}O_2 \rightleftharpoons O \qquad K_2 = a_8\left(\frac{P_P}{P_0 a_7 N_P}\right)^{0,5} \qquad K_2 = exp\left(\left(\bar{G}_{T,O} - 0{,}5\bar{G}_{T,O_2}\right)/R_u T\right) \tag{10}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad K_3 = \frac{a_1 a_4}{a_2 a_3} \qquad K_3 = exp\left(\left(\bar{G}_{T,CO_2} + \bar{G}_{T,H_2} - \bar{G}_{T,CO} - \bar{G}_{T,H_2O}\right)/R_u T\right) \tag{11}$$

$$\frac{1}{2}H_2 \rightleftharpoons H \qquad K_4 = a_5\left(\frac{P_P}{P_0 a_4 N_P}\right)^{0,5} \qquad K_4 = exp\left(\left(\bar{G}_{T,H} - 0{,}5\bar{G}_{T,H_2}\right)/R_u T\right) \tag{12}$$

$$\frac{1}{2}H_2 + \frac{1}{2}O_2 \rightleftharpoons OH \qquad K_5 = \frac{a_6}{a_4^{0,5} a_7^{0,5}} \qquad K_5 = exp\left(\left(\bar{G}_{T,OH} - 0{,}5\bar{G}_{T,H_2} - 0{,}5\bar{G}_{T,O_2}\right)/R_u T\right) \tag{13}$$

$$O_2 + N_2 \rightleftharpoons 2NO \qquad K_6 = \frac{a_{10}^2}{a_7 a_9} \qquad K_6 = exp\left(\left(2\bar{G}_{T,NO} - \bar{G}_{T,O_2} - \bar{G}_{T,N_2}\right)/R_u T\right) \tag{14}$$

$$C + 2H_2 \rightleftharpoons CH_4 \qquad K_7 = \frac{a_6}{a_4^2}\left(\frac{P_P}{P_0 N_P}\right)^{-1} \qquad K_7 = exp\left(\left(\bar{G}_{T,CH_4} - 2\bar{G}_{T,H_2}\right)/R_u T\right) \tag{15}$$

Notice that equation 9-15 introduces one more unknown 12 temperature therefore one more equation is required and it comes from energy balance.

## 2.1.Energy balance

It is necessary to know the reaction temperature. To obtain this value, the first Law of the thermodynamics or energy balance is performed.

$$\sum_{React.} N_j \bar{h}^o_{f,j} = \sum_{Prod.} N_i \bar{h}_i \tag{16}$$

Where $\bar{h}^o_{f,j}$ is the enthalpy of formation in kJ/kmol for all reactants in the reference state (298 K, 1 atm)

The Eq.(17) establishes a relation between pressure of the products ($P_P$) and pressure of the reagents ($P_R$), the constant ($\gamma$) relates the constant pressure and constant volume processes. This constant will have the value zero for constant pressure processes and one for constant volume processes.

$$P_P = \gamma P_R \left(\frac{N_P T_P}{N_R T_R} - 1\right) + P_R \tag{17}$$

It is more suitable for developing the computer code if all thermodynamic properties, which are functions of temperature, are described in terms of polynomial equations. Thus, data from the technical memorandum TAE 960 (Burcat and Ruscic, 2005) are used to calculate all thermodynamic properties in this model. From this data resource, the heat capacity at constant pressure for the standard state was formulated in a polynomial equation of order four (five constants).

$$\frac{\bar{c}_P}{Ru} = c_1 + c_2 T + c_3 T^2 + c_4 T^3 + c_5 T^4 \tag{18}$$

For the enthalpy and the entropy, they are defined in polynomials with six constants,

$$\frac{\bar{h}_T}{RuT} = c_1 + \frac{c_2 T}{2} + \frac{c_3 T^2}{3} + \frac{c_4 T^3}{4} + \frac{c_5 T^4}{5} + \frac{c_6}{T} \tag{19}$$

$$\frac{\bar{s}_T}{Ru} = c_1 lnT + c_2 T + \frac{c_3 T^2}{2} + \frac{c_4 T^3}{3} + \frac{c_5 T^4}{4} + c_7 \tag{20}$$

Gibbs free energies were evaluated by:

$$\bar{g}_T = \bar{h}_T - T\bar{s}_T \tag{21}$$

The enthalpy of formation was obtained for the fuel reactant as below:

$$\bar{h}_{fuel} = HHV m_{f,s} + x\,\bar{h}^o_{f,CO_2} + \frac{y}{2}\bar{h}^o_{f,H_2O} + w\bar{h}^o_{f,NO} + v\bar{h}^o_{f,SO_2} \quad \left[\frac{kJ}{kg}\right] \tag{22}$$

Where $\bar{h}^o_{f,i}$ are the products after an complete combustion of the fuel, and HHV is the higher heating value of the fuel. The HHV of fuel will be calculated with the formula presented by (Channiwala, 2002), that is:

$$HHV = 349{,}1C + 1178{,}3H + 100{,}5S - 103{,}4O - 15{,}1N - 21{,}1A \quad \left[\frac{kJ}{kg}\right] \tag{23}$$

The lower heating value of the fuel can be calculated by Eq.(24):

$$LHV = HHV\frac{m_{f,s}}{m_{f,m}} - \left(\frac{m_{H_2O,c} + m_{H_2O,f}}{m_{f,m}}\right) h_{lv} \quad \left[\frac{kJ}{kg}\right] \tag{24}$$

Where $m_{f,m}$ is the mass of fuel with moisture content, $h_{lv}$ is the enthalpy of vaporization of water at flue pressure and $m_{H_2O,c}$ is the mass of water formed after the complete combustion of the fuel, defined as:

$$m_{H_2O,c} = \frac{y}{2} M_{H_2O} \tag{25}$$

All equations shown above were solved using EES software. EES uses a variant of Newton's method to solve systems of non-linear algebraic equations. The Jacobian matrix needed in Newton's method is evaluated numerically at each iteration. Sparse matrix techniques are employed to improve calculation efficiency and permit rather large problems to be solved in the limited memory of a microcomputer.

## 3. VALIDATION OF THE MODEL

The model developed in this study was tested by comparing the calculation results with the computer program CEA (Gordon and MaBride, 1994) for combustion and gasification processes. The elementary analysis and HHV of açaí seeds used in the simulation processes are given in Table 1.

Table 1. Elementary analysis and HHV of açaí seeds

| Elementary analysis dry base | |
|---|---|
| C | 46,60 |
| H | 6,52 |
| O | 44,11 |
| N | 1,06 |
| S | 0,84 |
| Ash | 0,87 |
| HHV [MJ/kg] | 16822,56 |

Calculation with the program CEA was performed assuming the molecular formula of the fuel $C_{3,913}H_{6,528}O_{2,781}N_{0,076401}S_{0,026513}$, and its enthalpy of formation $\bar{h}_{fuel} = -791783,68\ kJ/kg$

In the combustion process the gas composition is calculated for the equivalent ratio varied from 0.6 to 1.3, the Fig. 1 showed good accuracy with the model developed in the program CEA. Only the temperature shows a small variation of 0.15% for the equivalent ratio from 1 to 1.3.

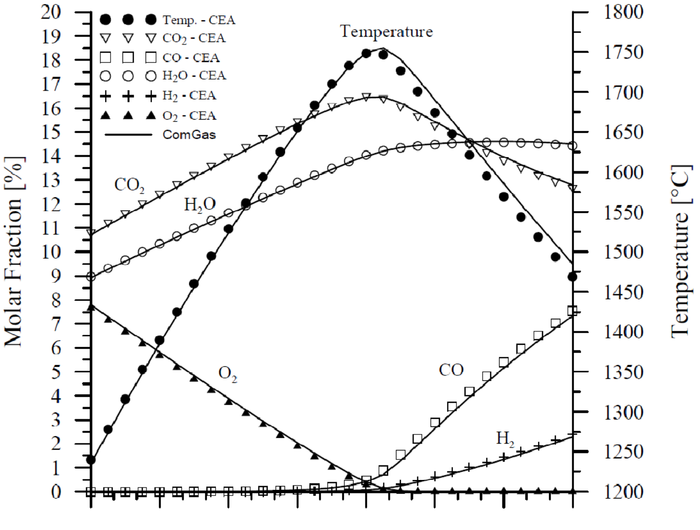

Figure 1. Comparison of the model predicted and program CEA for combustion process (pressure: 1 atm)

For the gasification process the gas composition is calculated for the equivalence ratio from 2 to 4. In this case the predicted values are CO, $CO_2$, $H_2$, $CH_4$ and temperature (Fig. 2). The values of CO, $CO_2$ and $CH_4$ calculated by the model have a good approach compared with the program CEA, but variations exist of 1.2% for the temperature and of

2.05% for $H_2$. The authors considered the differences on combustion and gasification as a consequent of the numerical approach the minimization of Gibbs free energy and ComGas uses the classical approach through Gibbs number.

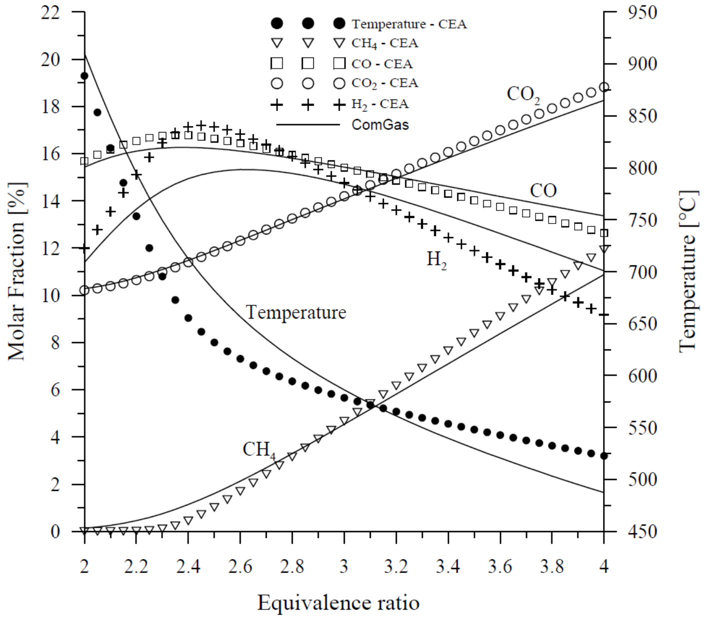

Figure 2. Comparison of the model predicted and program CEA for gasification process (pressure: 1 atm)

Following the model developed in this study was tested by comparing the calculations results from ComGas with the data from literature for gasification processes. Nine experimental results from "Jayah *et al.* (2003)" were used to compare with simulation results of this model. The comparison was done by setting the temperature used for the developed model fixed at 1100K as reported by "Jayah *et al.* (2003)". Table 2 shows the comparisons of results between ComGas and the experimental data. The error in this comparison is estimated by the root-mean-square (RMS), defined as

$$RMS = \sqrt{\frac{\sum_i^n (Exp_i - Mod_i)^2}{D}} \tag{26}$$

where *Exp* is the value from the experimental results, *Mod* is the predicted value from ComGas, and *D* is the number of data.

Table 2. Comparison of the model predicted with the experimental data from "Jayah *et al.* (2003)"

| N° | RM [%] | Φ | Model CO [%] | Exp. CO [%] | Model $H_2$ [%] | Exp. $H_2$ [%] | Model $CH_4$ [%] | Exp. $CH_4$ [%] | RMS error |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 18,5 | 3,06 | 19,7 | 19,6 | 20,4 | 17,2 | 0,8 | 1,4 | 1,87 |
| 2 | 16,0 | 2,82 | 19,0 | 20,2 | 18,8 | 18,3 | 0,7 | 1,1 | 0,79 |
| 3 | 14,7 | 2,62 | 18,0 | 19,4 | 17,5 | 17,2 | 0,6 | 1,1 | 0,86 |
| 4 | 16,0 | 3,17 | 21,1 | 18,4 | 20,8 | 17,0 | 0,8 | 1,3 | 2,71 |
| 5 | 15,2 | 2,93 | 20,0 | 19,7 | 19,4 | 13,2 | 0,7 | 1,3 | 3,62 |
| 6 | 14,0 | 2,71 | 18,9 | 18,9 | 18,0 | 12,5 | 0,6 | 1,2 | 3,20 |
| 7 | 14,7 | 3,34 | 22,5 | 19,1 | 21,6 | 15,5 | 0,9 | 1,1 | 4,03 |
| 8 | 13,8 | 3,04 | 21,1 | 22,1 | 20,0 | 12,7 | 0,8 | 1,3 | 4,25 |
| 9 | 12,5 | 2,63 | 18,7 | 19,1 | 17,4 | 13,0 | 0,6 | 1,2 | 2,58 |

Table 2 show that the predicted results generally agree with other experimental data, except for the case of $CH_4$. The slightly difference in the results may result from the assumptions defined in simplifying the model, such as all gases are assumed to be ideal, no residue, absence of tar. The interesting points in the comparisons are the amount of $H_2$ and $CH_4$.

The model predicted higher amounts of $H_2$, but the predicted amounts of $CH_4$ are lower than all experimental data. It is important to note that equilibrium models from the literatures reviewed "Li *et al*. (2001)", "Altafini *et al*. (2003)" and "Zainal *et al*. (2001)" predicted the $H_2$ concentration higher and the $CH_4$ concentration lower than the measured data from experiment. In calibrating the model of "Jayah *et al.* (2003)", the amount of methane predicted was adjusted in such a way that it was equal to the amount of methane measured in the product gas.

## 3. CONCLUSION

ComGas was developed to solve chemical equilibrium problems for combustion and gasification processes and it is currently available from "Zárate *et al.* (2008)". Students and educators can use such program to graphically specify and solve complex chemical equilibrium problems for combustion and gasification without needing to install, and navigate an awkward command line interface intrinsic to existing codes, pay expensive licensing fees, or struggle with open-source software compilation. ComGas allow the user to define the fuel composition (by elementary analysis) and the product species. For a given equivalent ratio and pressure, the ComGas calculates the equilibrium composition. On the other hand, the results of this model in relation to other similar programmes ensure its efficiency. Thus, the proposed program is perfectly adequate for the calculations of the combustion and gasification products.

## 3. ACKNOWLEDGEMENTS

We want to acknowledge CNPQ and EBMA to make this work possible.

## 4. REFERENCES

Altafini CR, Wander PR, Barreto RM. Prediction of the working parameters of a wood waste gasifier through an equilibrium model. Energy Convers Manage 2003;44:2763–77

Burcat A, Ruscic B. Third Millennium Ideal Gas and Condensed Phase, Thermochemical Database for Combustion with Updates from Active Thermochemical Tables. The University of Chicago for the U. S. Department of Energy, 2005

Channiwala SA, Parikh PP. A unified correlation for estimating HHV of solid, liquid, and gaseous fuels. Fuel 2002;81(8):1051–63.

De Souza-Santos ML. Solid fuels combustion and gasification: modeling, simulation, and equipment operation. New York: Marcel Dekker; 2004.

Gordon S, MaBride BJ. Computer program for calculation of complex chemical equilibrium compositions with applications; I. analysis. NASA Reference Publication 1311. Cleveland (OH): NASA; 1994.

Jarungthammachote S, Dutta A. Thermodynamic equilibrium model and second law analysis of a downdraft waste gasifier. Energy 2007;32:1660–9.

Jayah, T.H., Aye, L., Fuller, R.J. and Stewart, D.F. (2003) Computer simulation of a downdraft wood gasifier for tea drying, Biomass Bioenergy, 25, pp. 459-469.

Kee, R.J., Rupley, F.M., Meeks, E., Miller, J.A., CHEMKIN -III: A Fortran Chemical Kinetics Package for the Analysis of Gas-Phase Chemical and Plasma Kinetics, Sandia National Laboratories, Livermore, CA, 1996

Klein SA, Alvarado FL. EES-Engineering Equation Solver for microsoft windows operating systems. F-Chart Software, 2004.

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

McBride BJ, Gordon S, Reno MA. Coefficients for calculating thermodynamic and transport properties of individual species. NASA Technical Memorandum 4513, NASA; 1993

Reynolds, W. C., The Element-Potential Method for Chemical Equilibrium Analysis: Implementation in the Interactive program STANJAN. Unnumbered Report, Department of Mechanical Engineering, Stanford University, Palo Alto, CA, 1986.

Zainal ZA, Ali R, Lean CH, Seetharamu KN. Prediction of the performance of a downdraft gasifier using equilibrium modeling for different biomass materials. Energy Convers Manage 2001;42: 1499–515.

Zárate H.M.R., Itai Y. and Nogueira M.F.M, ComGas v1.2 - Programa para combustão e gasificação. Universidade Federal do Pára (UFPA). EBMA. 2008. http://www.ppgem.ufpa.br/uploaded/ComGas_v1.2.rar.

## 5. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.