23rd ABCM International Congress of Mechanical Engineering
December 6-11, 2015, Rio de Janeiro, RJ, Brazil

BRAZILIAN BIOMASS GASIFICATION: A NUMERICAL SIMULATION OF BIOMASS GASIFICATION FROM DIFFERENT BIOMES

Mara Rúbia da Silva Miranda [1]
Fábio Cordeiro de Lisboa[2]
Alexandre Caires Rodrigues[3]
UnB - Campus Universitário Darcy Ribeiro, Brasília - DF, 70910-900
[1] mara_miranda20@yahoo.com.br; [2] fabiodelisboa@gmail.com, [3] alexandrecaires@gmail.com

Abstract. *The use of biomass as an energy source has increased lately. The reason for this fact lies in the constant generation of agro-industrial and forest wastes. An environmentally friendly way to handle this residue is the energy recovery through conversion processes. Several studies have been conducted to find a more efficient process. In this context, this paper has as main objective to model the reactions of the gasification process, in order to estimate the concentrations of gases and the high heat value (HHV). Due to the increasing interest in biomass gasification, several models have been proposed to explain and understand this complex process. These thermodynamic models are essential to understanding the influence of parameters involved and indicate which are the most important and which ones interfere directly in the process energy efficiency. Thus, a sensitivity analysis was performed to relate the molar concentrations of O_2, H_2, CO, CO_2 and the temperature in the reaction zone. It was also calculated the equilibrium constant K. Finally, limiting parameters for different gasification plants were defined. Using the Engineering Equation Solver (EES), a routine based on chemical kinect law of mass action was created. As input, the elemental analyzes of three different biomes biomass were used: fruit of macauba, assai seeds and eucalyptus wood. As a result, there was no significant difference in CO fractions and high heat value of the biomass varying the equivalence ratio of 2.8 to 3.2, in the best results, but the mass fractions of H_2 was possible that there is a significant upward trend in the case of eucalyptus is compared to assai and macauba. Finally, it was found that the three biomasses are very similar, so it becomes feasible to use them for the production of syngas, since the waste is a very important factor for the choice of biomass because of existing large quantity worldwide.*
Keywords: *Biomass, Gasification, Chemical Kinect*

1. INTRODUCTION

The use of biomass as an energy source has increased in recent years and the biggest justification for this fact is the constant generation of this source, such as industrial and forestry wastes. One way to reduce the environment pollution is generating energy through existing conversion processes. Several studies have been done to find a better process in the energy efficiency aspect. Aiming then study the gasification, this article has general purpose of modeling the gasification process reactions in order to calculate the concentrations of the gases and the high heat value HHV.

Due to the growing interest in gasification of biomass, several models have been proposed to explain and understand this complex process. For this study, optimizations, simulations and analysis of gasification processes have been performed. These thermodynamic models are essential to understanding the influence of parameters and indicate what are the most important and that interfere directly in energy efficiency. Thus the specific objective is perform a sensitivity analysis considering the amount of air and water into the reactants and varying the equivalence ratio of air and fuel. Calculate the equilibrium constant, taking the molar concentrations, and finally, compare the biomasses and finding the better.

Gasification is the partial thermal oxidation which results in a high proportion of gaseous products (CO_2, H_2O, CO, H_2 and gaseous hydrocarbons), small amounts of solid carbon, ash and condensable compounds like tar and oils. The supplied gasification agents for the reaction can be air, steam or oxygen. The gas produced can be converted into marketable products and therefore has a greater versatility of use of the biomass. These are complex thermochemical processes, including gasification, where the amount of heat dissipated in the system is key to greater energy efficiency. Other factors, such as the gasification agents also can influence the temperature in the process. So to a higher yield on gasification, kinetic modeling is a tool that helps in the estimate of input parameters (Puig-Arnavat *et al.*, 2010). In this context, this article is justified by calculating the main factors that interfere directly in the gasification process.

The importance of providing the results and evaluate the gasification plant and its operation as a whole can minimize losses and increase energy efficiency, which is the goal of the studies of these conversion processes. Throughout the article is described the principles of gasification technology for understanding the final results and the importance of the parameters in this process.

2. GASIFICATION AND KINECTS MODELS

2.1 Gasification technology

The gasification of biomass involves several chemical reactions and the heat and mass transfer processes. Gasification, as a whole, is the conversion of raw materials into gaseous fuel or raw material that can be burned to release energy or used for the production of chemical products of value to the market (Basu, 2010). This process requires a gasification agent, air, oxygen or steam, to rearrange the molecular structure of the raw material and convert it into a gaseous fuel with a higher proportion of hydrogen-carbon. In a typical gasifier the drying occurs at a temperature below 150°C, pyrolysis occurs in the temperature interval 150-700°C, oxidation occurs 700-1500°C and reduction occurs between 800-1100°C (Basu, 2006) and (Bridgwater e Bridge, 1991).

Within the thermochemical route, gasification of biomass is an important technology and being widely studied and in some countries, is already being used due to its ability to handle wide variety of biomass feedstocks. In this context gasification technology is one of the best alternatives for reuse of solid waste. The process can be represented by the following steps global reactions (Mckendry, 2002).

1) Heating and drying of the biomass: At this stage, the moisture content of the biomass ranges from 5% to 35% is reduced.
2) Pyrolysis of biomass (devolatilization): This step consists in thermal decomposition of the biomass in the absence of oxygen or air. In this process, the volatile material from the biomass is reduced and this results in outgassing of hydrocarbons from biomass. These gaseous hydrocarbons can condense at a sufficiently low temperature to generate liquid tars.
3) Oxidation: This is a reaction between the solid carbonized biomass and oxygen, which results in the formation of CO2. Hydrogen present in biomass is also oxidized to generate water.
4) Reduction: In the absence (or presence of stoichiometric) of oxygen, various reduction reactions occur at a temperature of 800-1100°C range. These reactions are mainly endothermic and the main reactions in this phase are:

Water-gas reaction: $C + H_2O \rightarrow CO + H_2 \ +131.4kJ/mol\,carbono$ (1)

Bounded reaction: $C + CO_2 \rightarrow 2CO \ +172.58kJ/mol\,carbono$ (2)

Shift reaction: $CO_2 + H_2 \rightarrow CO + H_2O \ -41.98kJ/mol$ (3)

Methane reaction: $C + 2H_2 \rightarrow CH_4 \ -74.90kJ/mol\,carbono$ (4)

The gas composition obtained by gasification technology depends on many parameters, such as pressure, temperature, moisture content, gasification agent, amongst others. The gasification agents can be air, pure O_2, steam, CO_2 or mixtures thereof. The air as an inexpensive and widely used gasifying agent contains a large amount of nitrogen, which reduces the HHV of the produced syngas. If pure O_2 is used as the gasification agent, the HHV of gas will increase, but also the operating costs increase due to O_2 production costs. Table 1 provided average values of the HHV of the fuel gas to processes performed with air, pure oxygen and water vapor as gasification agent (Belgiorno *et al.*, 2003).

Table 1. HHV of gasification processes.

Process	Gasifying agents	HHV ($MJ.Nm^{-3}$)
Direct gasification	Air	4-7
Oxygen gasification	Oxygen	10-12
Indirect gasification	Steam	15-20

2.2 Kinects models

The kinetic models provide information on the kinetic mechanism in the conversion of biomass. Understanding the kinetics is critical to not only evaluate the parameters and improve the gasifier performance, but also choose the best design according efficiency.

Currently, there are many works (Giltrap *et al.*, 2003), (Wang e Kinoshita, 1993), (Jarungthammachote e Dutta, 2008), (Gautam *et al.*, 2010), (Huang e Ramaswamy, 2009), (Barman *et al.*, 2012), (Puig-Arnavat *et al.*, 2012) and (Melgar *et al.*, 2007) on the kinetic modeling aimed at finding the best performance of a gasifier. Many models of reduction zone in a downdraft gasifier were made in order to predict the composition of the gas produced in operation at steady state, adopting chemical kinetic expressions. The accuracy of the model is limited by the availability of data on the initial conditions at the top of the reduction zone. Pyrolysis reactions are not considered because the number of

possible pyrolysis products, along with all the possible reactions and intermediate products, would do very complex model. Thus, the authors assumed that all incoming air oxygen is burned to CO_2 and resulting pyrolysis products are completely cracked. The solid carbon-carbon way is considered to be present throughout the reduction region. Another important parameter is the reactivity of the coal factor, which the authors consider it as constant over the reduction zone. Through these models it is possible to investigate the effects of the parameters including developing a non-stoichiometric models and the effects of moisture and temperature on the quality of the gas.

Ghassemi e Shahsavan-Markadeh (2014) proposed a model using the Gibbs energy where analyzing the effect of O_2 with air was noticed that the increase of the proportion of A/O (air / oxygen) reflects the increased HHV of the syngas. Regarding equivalence ratio (ϕ) realized in its results that the maximum gas efficiency occurs at a rate of A/O higher, but with a ratio of average equity, and therefore deduced that for optimal performance in gasification, the key would be a higher rate of A/O with lower oxygen consumption. The equivalence ratio is defined according to the authors as the real oxygen ratio is equivalent to the stoichiometric amount in the gasification process. These authors also observed the influence of moisture. The moisture content of various biomass is remarkable and can also affect the performance of the gasification process. In the proposed model, the authors realized that the lower moisture content leads to a higher gross calorific value. It is known that the moisture content of the biomass significantly affect gasification temperature because the heat required for evaporation of moisture and therefore deserves attention as an important parameter. In addition, they analyzed the effect of temperature. The temperature influences several aspects of the process and therefore the quality of synthesis gas. The authors observed that increasing the temperature increases the gas efficiency, and for temperatures above 700°C the gas efficiency is not as affected by temperature and thus can be neglected.

As can be seen there are numerous jobs with the proposal of analyzing and understanding the best outcome for the gasifiers. Godinho (2006) found the constant methane reaction balance, this reaction is exothermic, so that formation of products is favored at low temperatures where the reaction equilibrium constants are: $3.25x10^{-1}$, $9.83x10^{-2}$ and $3.67x10^{-2}$ at $527°C$, $627°C$ and $727°C$ respectively.

3. MATERIALS AND METHODS

To simulation of gasification are used scripts based on the law of mass action, mathematical model that explains and predicts behavior of solutions in dynamic equilibrium. This model can be described by the aspect of balance, where the expressions for the equilibrium constant are established and the kinetic aspect related to elementary reactions, where rates of a reaction proceed only from a transition state and is proportional to the product of the concentrations of participating molecules.

Using equivalent equation of Biomass CxHyOz, and the general reaction, sets out the initial conditions of the process

$$C_xH_yO_z + a(O_2 + 3{,}76N_2) + wH_2O = bCO + dH_2O + eN_2 + fO_2 + lH_2 + kCH_4 \ , \tag{5}$$

solid biomass react with theoretical air fraction "*a*" at 300K and 1 bar. To calculate the theoretical air fraction will need to calculate the stoichiometry of the reaction by the equation 6

$$C_xH_yO_z + a(O_2 + 3{,}76N_2) = b_{stoic}CO_2 + c_{stoic}H_2O + e_{stoic}N_2 \ , \tag{6}$$

the equivalence ratio ϕ is defined as shown in equation 7, and sets a ratio enters the amount of air and fuel in the reaction relative to the stoichiometric amount required

$$\Phi = \frac{m_{biomassa}/m_{air}}{m_{biomassa_{st}}m_{air\_st}/m_{air\_st}} . \tag{7}$$

For calculation purposes is considered the molar fraction of methane produced equal to k = 0.017 and the amount of water added in the reactants w = 0.1, assuming the low methane production in the reaction and adding a small amount of water in the form of reagents to improve the production of hydrogen. The gas constant is R = 8.314 kJ/kmol-K. The enthalpy of formation is related to the enthalpy difference of products and reagents for calculation purposes are used the formation enthalpy values calculated by Baker (2008). The enthalpy of formation of water is considered 285,5kJ/kmol, of eucalyptus wood is -179316,84 kJ/kmol, of assai seeds is -41524,97 kJ/kmol and of macauba seeds is -439467,04 kJ/kmol. The Gibbs number is calculated by equation 8

$$g = h - (T.s) \ , \tag{8}$$

and the function of Gibbs formation by equation 9

$$\bar{g}^{0}{}_{i,T} = \bar{g}^{0}{}_{i}(T) - \sum_{j\,elementos} \upsilon_j \bar{g}_j{}^{0}(T)\,. \tag{9}$$

For the chemical balance, variation in the number of Gibbs

$$\Delta G_T^0 = -R_u T \ln K_p\ , \tag{10}$$

when the constants of equilibrium is given by

$$K_p = \exp(\frac{-\Delta G_T^0}{R_u T}). \tag{11}$$

As the main gasification reactions are shown in equations 1 and 2 are used for the calculation of the equilibrium constants *K1* and *K2* the equations 12 and 13

$$K_1 = \frac{y_{CO}}{y_{CO_2}} . \sqrt{y_{O_2} \frac{P}{P_{ref}}}\ , \tag{12}$$

$$K_2 = \frac{y_{H_2O}}{y_{H_2} \sqrt{y_{O_2} \frac{P}{P_{ref}}}}\ . \tag{13}$$

Thus the variation in the number of Gibbs for both reactions are given by equations:

$$\Delta G_1^0 = 0.5 g_{O_2}^0 + g_{CO}^0 - g_{CO_2}^0\ , \tag{12}$$

$$\Delta G_2^0 = g_{H_2O}^0 - g_{H_2}^0 - 0.5 g_{O_2}^0\ , \tag{13}$$

$$\Delta G_1^0 = -R \times T \times \ln(K_1)\ , \tag{14}$$

$$\Delta G_2^0 = -R \times T \times \ln(K_2)\ . \tag{15}$$

The enthalpy of the reactants and products are given respectively by equations 16 and 17:

$$H_R = h_{f(C_x H_y O_z)} + a h_{f(O_2)} + 3.76 a h_{f(N_2)} + w h_{f(H_2O)}\ , \tag{16}$$

$$HP = b h_{(CO_2)} + c h_{(CO)} + d h_{(H_2O)} + e h_{(N_2)} + f h_{(O_2)} + l h_{(H_2)} + k h_{(CH_4)}\ . \tag{17}$$

As the enthalpy of the products is equal to the enthalpy of the reactants, a formulation of 52 equations for 52 variables is achieved making it possible solution. When the program returns thin values of mass fractions of hydrogen, carbon monoxide and methane. With these values you can calculate the high heat value (HHV) using equation 18 below.

$$PCS = 33883 \times y_{H_2} + 2412 \times y_{CO} + 13249 \times y_{CH_4} \tag{18}$$

The equivalent chemical formulas used for simulation were obtained by elementary analysis using a Perkin-Elmer 2400 (series 2) CHN analyzer The PE 2400 which is specified to achieve results within 0.3% on pure standard organic materials where sample size is in the range of 1 to 3 milligrams. For these experiments were used 3 milligrams for each biomass, in order to find percentage of carbon (%C), hydrogen (%H) and nitrogen (% N). The percentage of oxygen (% O) was found by difference.

Following are presented the results obtained by applying this methodology.

4. RESULTS AND DISCUSSIONS

The results of elementary analysis can be shown in the Table 2 below. For each biomass was measured the mass fraction of each element, and then, calculated the equivalent formula of biomass, who will be used in the next step to find correct composition of syngas.

Table 2 - The chemical equivalent formula for each biomass

Analysis	Eucalyptus wood	Assai seed	Macauba seed
Carbon (%C)	48.65 ± 0.3%	47.8 ± 0.3%	48.38 ± 0.3%
Hydrogen (%H)	6.55 ± 0.3%	5.57 ± 0.3%	6.14 ± 0.3%
Nitrogen (%N)	0.10 ± 0.3%	0.01 ± 0.3%	0.41 ± 0.3%
Oxygen (%O)	44.66 ± 0.3%	46.19 ± 0.3%	44.82 ± 0.3%
Ashes (%A)	0.04 ± 0.3%	0.44 ± 0.3%	0.25 ± 0.3%
Equivalent formula	$C_{4.050}H_{6.499}O_{2.791}N_{0.001}$	$C_{3.980}H_{5.526}O_{2.887}N_{0.001}$	$C_{4.028}H_{6.092}O_{2.801}N_{0.029}$

Simulation of gasification by solving the mathematical model described in item 3, used air as gasifying agent with 0.21 (O_2) + 0.79 (N_2). The simulation search the synthesis gas concentrations composed of CO, H_2 and CH_4, predicting then the HHV of the gas to the end of the process, as well as the cold gas efficiency. The biomass equivalent formula (Table 2) used as input data as well as the values of mass fraction of water in reacts, mass fraction of methane in products, enthalpy of formation of water and biomass.

After run, the script returns the values of mass fraction of products of reaction. These data compiled in graphs, as shown in the Figures 1 and 2. In Figure 1 it is not possible to note a significant difference between the results of CO mass fraction of each sample, but assai seed was a little bit higher than macauba seed and eucalyptus wood. In the Figure 2 the difference was greater, and the mass fraction of H2 eucalyptus was higher than that of the others biomass. Both in Figure 1 and Figure 2 concluded that exist a limit to production syngas, and its limits depends of equivalence ratio in reaction.

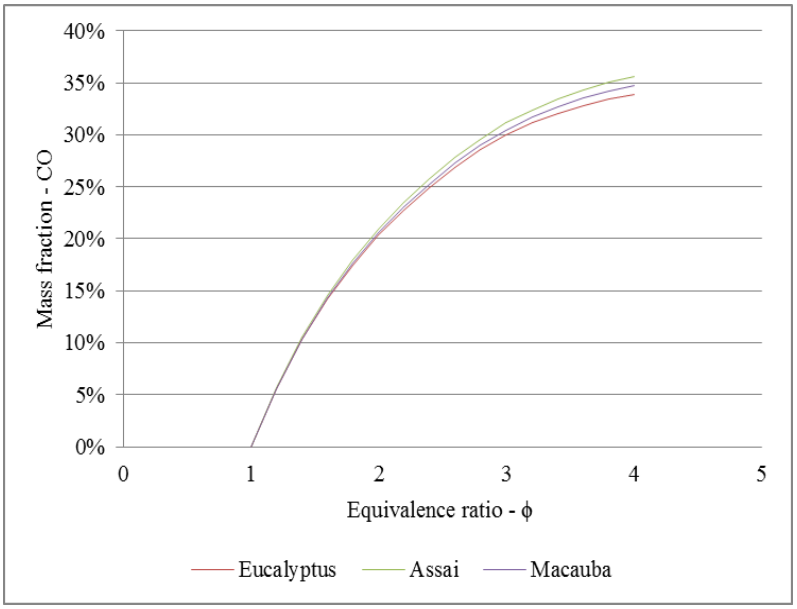

Figure 1. Syngas mass fraction of CO

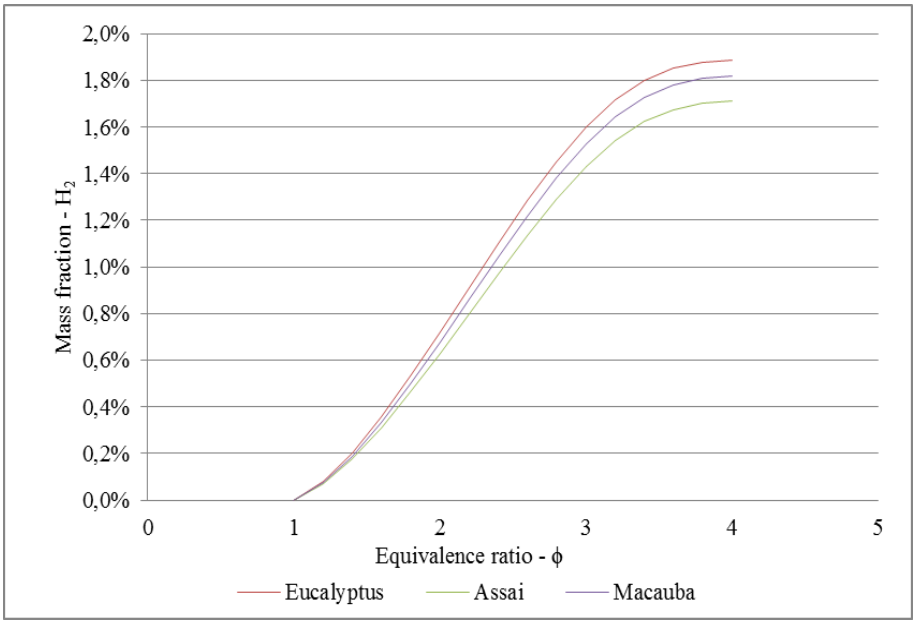

Figure 2. Syngas mass fraction of H_2

Using the equation 18, is possible to calculate the syngas HHV (Figure 3). The area showed in the picture shows the region of gasification, according Bridgwater e Bridge (1991) gasification occurs between 800°C and 1100°C.

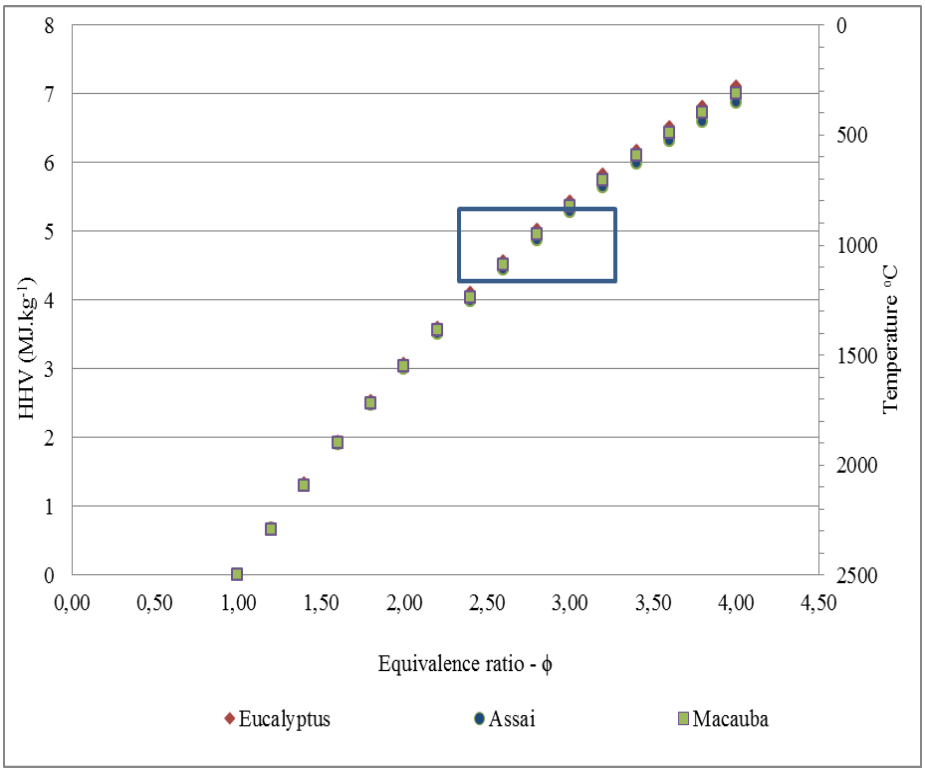

Figure 3. Calculated HHV for syngas made by biomass gasification.

In Figure 3 it was concluded that the results of HHV were very close for these biomass, but for equivalence ratio after 2.5 is possible to notice an appreciable difference eucalyptus HHV. In this region the reaction are close to maximum production of CO and H_2, as showed in graph of Figures 1 and 2.

The results (Table 3) are adherent to the literature values shown in Table 1 cited by Belgiorno et al. (2003) where the HHV ranges for each type of gasifying agent. Table 3 summarize the results of simulation, note that using O_2 as gasifying agent the syngas has much higher HHV when it was using the air. However, it is important to remember that O_2 is more expensive then is necessary to conduct a more detailed study of the characteristics of biomass together with the input parameters more efficiently to enable the use of O_2 and thereby obtain higher yields and compensate for its use. For Belgiorno et al. (2003), the use of oxygen for gasification makes the process expensive, and the air typically used for procedures up to about 50 MW. The authors also reinforce the view and states that the direct gasification with pure oxygen has the same advantages of indirect gasification processes. However, the cost of oxygen production is estimated at more than 20% of the total cost of the electricity produced. Thus, it is also important to consider the economic factors.

Table 3. Simulation using air and O_2 as gasifying agents

	Maximum HHV ($MJ.Nm^{-3}$)		Temperature (°C)		Equivalence ratio	
Gasifying agent	Air	O_2	Air	O_2	Air	O_2
Eucalyptus	5.81	13.34	849.2	867.8	3.2	4
Assai	5.65	12.52	855.6	870.1	3.2	4
Macauba	5.74	13.04	855.4	873.4	3.2	4

5. CONCLUSIONS

These three biomass has a very close energy potential when it gets gasifying. Then eucalyptus wood, usually planted to supply the paper industry or charcoal in the iron industries southeastern and southern Brazil, can also be used to produce fuel gas. The industrial waste like assai seeds and Macauba seeds, can also help meet the energy demand of the regions center west and north, helping to balance the energy matrix with renewable energy production respecting the natural biomass of each species.

The use of computational tools to calculate the mass fractions involved in the reaction using chemical kinetics and the law of mass action, proved to be an important method for predicting the reaction results, saving time and project cost.

The method confirms the theory that the use of O2 as a gasifying agent improves the performance of the reaction to increase the syngas HHV. However the method is not able to simulate air mixtures with water or even the indirect gasification using only water as a gasifying agent. The method development and simulation script are recommendations for future work.

6. ACKNOWLEDGEMENTS

I thank the foundation to support of researches of Amazonas (FAPEAM), LabCat of Chemical Institute (IQ-UnB) for their support in carrying out this work.

7. REFERENCES

BARMAN, N. S.; GHOSH, S.; DE, S. Gasification of biomass in a fixed bed downdraft gasifier–A realistic model including tar. **Bioresource technology,** v. 107, p. 505-511, 2012. ISSN 0960-8524.

BASU, P. **Combustion and gasification in fluidized beds**. CRC press, 2006. ISBN 1420005154.

_____. **Biomass gasification and pyrolysis: practical design and theory**. Academic press, 2010. ISBN 0080961622.

BELGIORNO, V. et al. Energy from gasification of solid wastes. **Waste management,** v. 23, n. 1, p. 1-15, 2003. ISSN 0956-053X.

BRIDGWATER, A. V.; BRIDGE, S. A. A Review of Biomass Pyrolysis and Pyrolysis Technologies. **Biomass Pyrolysis Liquids. Upgrading and Utilisation**, p. 11-92, 1991. ISSN 185166565X.

GAUTAM, G.; ADHIKARI, S.; BHAVNANI, S. Estimation of biomass synthesis gas composition using equilibrium modeling. **Energy & Fuels,** v. 24, n. 4, p. 2692-2698, 2010. ISSN 0887-0624.

GHASSEMI, H.; SHAHSAVAN-MARKADEH, R. Effects of various operational parameters on biomass gasification process; a modified equilibrium model. **Energy Conversion and Management,** v. 79, p. 18-24, 2014. ISSN 0196-8904.

GILTRAP, D.; MCKIBBIN, R.; BARNES, G. A steady state model of gas-char reactions in a downdraft biomass gasifier. **Solar Energy,** v. 74, n. 1, p. 85-91, 2003. ISSN 0038-092X.

GODINHO, M. Gaseificação e combustão de resíduo sólidos da indústria calçadista. 2006.

HUANG, H.-J.; RAMASWAMY, S. Modeling biomass gasification using thermodynamic equilibrium approach. **Applied biochemistry and biotechnology,** v. 154, n. 1-3, p. 14-25, 2009. ISSN 0273-2289.

JARUNGTHAMMACHOTE, S.; DUTTA, A. Equilibrium modeling of gasification: Gibbs free energy minimization approach and its application to spouted bed and spout-fluid bed gasifiers. **Energy Conversion and Management,** v. 49, n. 6, p. 1345-1356, 2008. ISSN 0196-8904.

MCKENDRY, P. Energy production from biomass (part 3): gasification technologies. **Bioresource technology,** v. 83, n. 1, p. 55-63, 2002. ISSN 0960-8524.

MELGAR, A. et al. Thermochemical equilibrium modelling of a gasifying process. **Energy conversion and management,** v. 48, n. 1, p. 59-67, 2007. ISSN 0196-8904.

PUIG-ARNAVAT, M.; BRUNO, J. C.; CORONAS, A. Review and analysis of biomass gasification models. **Renewable and Sustainable Energy Reviews,** v. 14, n. 9, p. 2841-2851, 2010. ISSN 1364-0321.

PUIG-ARNAVAT, M.; BRUNO, J. C.; CORONAS, A. Modified thermodynamic equilibrium model for biomass gasification: a study of the influence of operating conditions. **Energy & Fuels,** v. 26, n. 2, p. 1385-1394, 2012. ISSN 0887-0624.

WANG, Y.; KINOSHITA, C. Kinetic model of biomass gasification. **Solar Energy,** v. 51, n. 1, p. 19-25, 1993. ISSN 0038-092X.

8. RESPONSIBILITY NOTICE

The author(s) is (are) the only responsible for the printed material included in this paper.