GASIFICATION OF BRAZILIAN BIOMASS AND SOLID FOSSIL FUELS: A COMPARATIVE STUDY OF FLUE GAS QUALITY FROM THE GIBBS FREE ENERGY MINIMIZATION APPROACH

Jhon Jairo Ramirez-Behainne, jhon@utfpr.edu.br
Department of Mechanical Engineering, Federal University of Technology (UTFPR), 84016-210, Ponta Grossa/PR, Brazil.

Luiz Guilherme dos Santos, luiz.santos@ufabc.edu.br
Center of Engineering, Modeling and Applied Social Sciences (CECS)- Federal University of ABC (UFABC), 09090-400, Santo André/SP, Brazil.

Abstract. *This work shows a comparative study about the flue gas quality obtained from the gasification process of several biomasses and solid fossil fuels by using the Gibbs free energy minimization approach. A mathematical algorithm was implanted in order to simulate the equilibrium composition of carbon monoxide, methane and hydrogen in the flue gas when Brazilian sugarcane bagasse, sawdust, rice husk, coal and oil shale are gasified. The model was applied aiming to determine the effects of the gasification equivalence ratio, fuel moisture, and reaction temperature on the volumetric composition of the flue gas and its higher heating value. Results of simulation for gasification equivalence ratios varying between 0.25 and 0.45, fuel moisture moving in the range of 10 to 30%, and temperature changing from 700 to 900ºC suggest that there is no significant difference for flue gas quality obtained from several biomass, but between renewable and fossil fuels. On the other hand, the behavior of the flue gas main components in relation to the analyzed factors was as expected when compared with data obtained from previous works. Results also indicated that the non-equilibrium model adopted can be useful for using in preliminary design of gasifiers.*

Keywords*: gasification, thermochemical equilibrium, biomass, coal.*

1. INTRODUCTION

Gasification is a thermochemical process that produces synthesis gas through the thermal degradation of usually a solid fuel involving its partial oxidation in a reducing atmosphere with the presence of air, oxygen and/or steam. Air-blown processes produce low calorific value gases with a typical higher heating value (HHV) of 4 to 7 MJ/Nm^3, while oxygen and steam-blown processes result in gases with a HHV of 10 to 18 MJ/Nm^3 (Schuster et al, 2001). Several types of models have been developed for simulating gasification systems, such as kinetic and equilibrium models. Unlike kinetic models that predict the progress and product composition at several positions along a reactor, an equilibrium model gives the maximum achievable yield of a desired product from a reacting system. So, although kinetic models provide essential information on mechanisms and rates, equilibrium models are valuable because they can predict thermodynamic limits as a guide to process design, evaluation and improvement (Li et al, 2001; Li et al, 2004).

There are two general and equivalent approaches to equilibrium modeling: stoichiometric, and non-stoichiometric. The former employs equilibrium constants of all constituent reactions, while the latter minimizes the Gibbs free energy subject to mass balance and non-negativity constraints. According Jarungthammachote and Dutta (2008), the non-stoichiometric approach is advantageous in more complex situations since no chemical reaction need be known to find the solution, which eases the simulation using computational tools. The objective of this study is to apply the non-stoichiometric equilibrium model based on the Gibbs free energy minimization approach in order to compare the composition and the energetic potential of flue gas obtained from gasification process of several Brazilian fossil and renewable fuels.

2. GASIFICATION MODEL

The thermochemical equilibrium of the gasification process for the biomass and solid fossil fuels analyzed in this work was modeled by using the Gibbs free energy minimization approach presented by Jarungthammachote and Dutta (2008). According this approach, at the equilibrium state, the total Gibbs free energy (G^t) for a thermodynamic system attains a minimum value, as indicated in Eq. (1):

$$G^t = \sum_{i=1}^{N} n_i \cdot \mu_i \tag{1}$$

In Eq. (1), n_i and μ_i are the number of moles and the chemical potential of species i, respectively. The chemical potential of species i is given by Eq. (2):

$$\mu_i = \bar{G}_i^0 + R.T.\ln(f_i/f_i^0) \tag{2}$$

where $\overline{G}_i^o$ is the standard Gibbs free energy of the species i; R is the universal gas constant, and T, the absolute temperature of the reaction system. f_i and f_i^o represent the fugacity of species i at system and standard conditions, respectively. In terms of pressure (P) and coefficient of fugacity (ϕ), the Eq. (3) can also be presented as:

$$\mu_i = \bar{G}_i^0 + R.T.\ln(\phi P_i/P^0) \tag{3}$$

If the gases of the gasification system are assumed as ideal gases at one atmosphere pressure, the Eq. (3) becomes:

$$\mu_i = \overline{\Delta G}_{f,i}^0 + R.T.\ln(y_i) \tag{4}$$

where y_i is the mole fraction of gas species i in the reaction mixture. $\Delta\overline{G}_{f,i}^o$ is the standard Gibbs free energy of formation of species i, which is set equal to zero for chemical elements. So, substituting Eq. (4) into Eq. (1):

$$G^t = \sum_{i=1}^{N} n_i\ \overline{\Delta G}_{f,i}^0 + \sum_{i=1}^{N} n_i\ RT\ln\left(\frac{n_i}{n_{tot}}\right) \tag{5}$$

The objective function G^t given by Eq. (5) is to be minimized by finding the n_i appropriated values for this proposal. A mathematical method usually applied for the minimization is the Lagrange multipliers, which involves the elemental balance of Eq. (6) as a constraint for the problem:

$$\sum_{i=1}^{N} a_{ij}\ n_i = A_j, \qquad j = 1,2,3,\ldots,k \tag{6}$$

where a_{ij} is the number of atoms of the jth element in a mole of the ith species. A_j is defined as the total number of atoms of the jth element in the reaction mixture. To form the Lagrangian function (L), the Lagrange multipliers, $\lambda_j = \lambda_l, \ldots, \lambda_k$, are used by multiplying with elemental balance constraints, and those terms are subtracted from G^t according Eq. (7):

$$L = G^t - \sum_{j=1}^{k} \lambda_j \left(\sum_{i=1}^{N} a_{ij} n_i - A_j\right) \tag{7}$$

The partial derivatives of Eq. (7) are set equal to zero in order to find the extreme point:

$$(\partial L/\partial n_i) = 0 \tag{8}$$

From Eq. (8) are obtained a total of i equations, and those are simultaneously solved with others that include the constraints defined by Eq. (6). So, if only the gaseous compounds CH_4, CO_2, CO, H_2O, H_2S, H_2 and N_2 are considered in an air-blown gasification process, the equations system formed by Eq. (9) through Eq. (15) needs to be solved considering also the constraints specified by Eq. (16) through Eq. (20):

$$\overline{\Delta G}_{f,CH_4}^0/RT + \ln\left(n_{CH_4}/n_{tot}\right) + \lambda_C/RT + 4\,\lambda_H/RT = 0 \tag{9}$$

$$\overline{\Delta G}_{f,CO_2}^0/RT + \ln\left(n_{CO_2}/n_{tot}\right) + \lambda_C/RT + 2\,\lambda_O/RT = 0 \tag{10}$$

$$\overline{\Delta G}_{f,CO}^0/RT + \ln\left(n_{CO}/n_{tot}\right) + \lambda_C/RT + \lambda_O/RT = 0 \tag{11}$$

$$\overline{\Delta G}_{f,H_2O}^0/RT + \ln\left(n_{H_2O}/n_{tot}\right) + 2\,\lambda_H/RT + \lambda_O/RT = 0 \tag{12}$$

$$\overline{\Delta G}_{f,H_2S}^0/RT + \ln\left(n_{H_2S}/n_{tot}\right) + 2\,\lambda_H/RT + \lambda_S/RT = 0 \tag{13}$$

$$\ln\left(n_{H_2}/n_{tot}\right) + 2\lambda_H/RT = 0 \tag{14}$$

$$\ln\left(n_{N_2}/n_{tot}\right) + 2\lambda_N/RT = 0 \tag{15}$$

$$n_{CH_4} + n_{CO} + n_{CO_2} = A_C \tag{16}$$

$$4n_{CH_4} + 2n_{H_2O} + 2n_{H_2} = A_H \tag{17}$$

$$n_{H_2O} + n_{CO} + 2n_{CO_2} = A_O \tag{18}$$

$$2n_{N_2} = A_N \tag{19}$$

$$n_{H_2S} = A_S \tag{20}$$

$$n_{CH_4} + n_{CO_2} + n_{CO} + n_{H_2O} + n_{H_2S} + n_{H_2} + n_{N_2} = n_{tot} \tag{21}$$

The *Engineering Equation Solver (EES*[TM]*)* software was used in order to determine the values of the 13 unknown variables in Eq. (9) through Eq. (21): n_{CH_4}, n_{CO_2}, n_{CO}, n_{H_2O}, n_{H_2S}, n_{H_2}, n_{N_2}, n_{tot}, λ_C, λ_H, λ_O, λ_N, λ_S. The A_j value of each element was previously obtained from the molar quantity present in reagents. In addition, the JANAF data base available in the *EES*[TM] was used for calculating the $\overline{\Delta G}_{f,i}^0$ values.

3. SIMULATION CONDITIONS

Table 1 shows the ultimate analysis of the fossil fuels (coal and oil-shale) and lignocellulosic biomasses (sugarcane bagasse, sawdust and rice husk) considered in simulations of the gasification process.

Table 1. Ultimate analysis of the Brazilian fuels studied in this work (% in dry mass basis) – Bizzo (2003)

Solid fuel[(1)]	Carbon	Hydrogen	Oxygen	Nitrogen	Sulphur	Ash
Coal	51.8	3.4	7.6	0.5	3.6	33.1
Oil-shale	33.5	2.4	3.8	0.1	2.8	57.4
Sugarcane bagasse	44,8	5,4	39.5	0,4	0.0	9.9
Sawdust	48.9	5.8	43.3	0.3	0.1	1,6
Rice husk	41.0	4.3	35.9	0.5	0.0	18.3

The simulations were carried out by taking into account only air as the gasifying medium, equivalence ratios (ratio of the fuel-to-oxidizer ratio to the stoichiometric fuel-to-oxidizer ratio) from 0.25 to 0.45, temperatures of 700 and 900°C, and fuel moisture of 10 and 30%. The ranges of equivalence ratio, temperature of reaction and fuel mixture were considered in the study because they represent approximately real conditions used in the air-blown gasifying process.

On the other hand, the higher heating value (HHV) of the flue gas, expressed in MJ/Nm³, was calculated according the Eq. (22), reported by Li *et al.* (2004):

$$HHV = 12.75(H_2) + 12.63(CO) + 39.82(CH_4) \tag{22}$$

where H_2, CO and CH_4 are the dry basis volumetric fractions of these components present in the flue gas.

4. RESULTS AND DISCUSSION

Figure 1 illustrates the CO yields in flue gas obtained from simulations when the variation in equivalence ratio, the gasification temperature and the fuel moisture were considered.
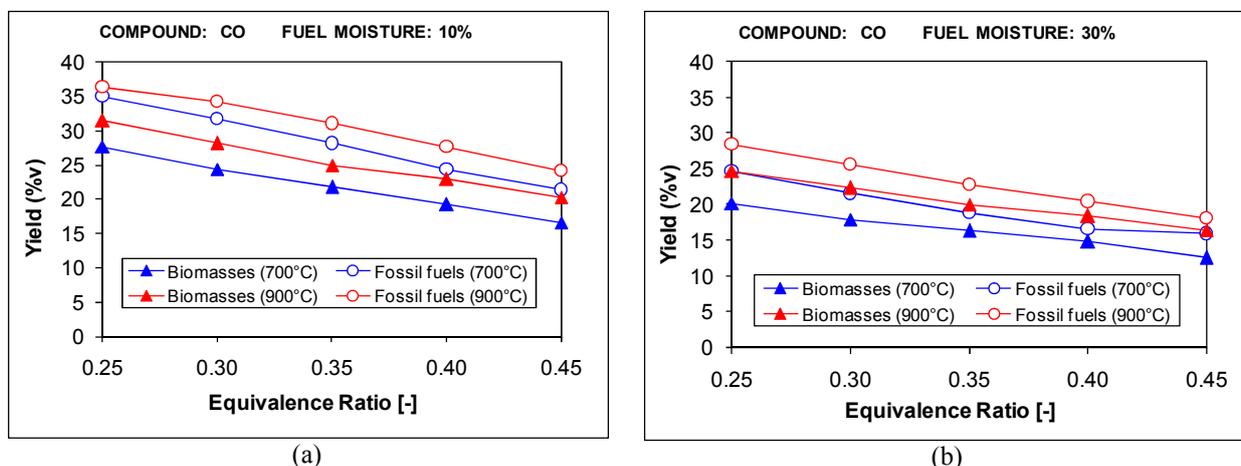
Figure 1. Volumetric yield of CO in flue gas (dry basis) in function of equivalence ratio and temperature reaction for 10% (a) and 30% (b) of fuel moisture.

As expected, the CO yield reduced when the equivalence ratio became higher. Higher equivalence ratios led to more CO conversion to CO_2 due to the increment of the oxygen participating in the actual reaction. In addition, was also noted that the gasification temperature enhanced the CO presence in flue gas, which is explained by the tendency of the CO formation at elevated temperatures according the Boudouard reaction (Basu, 2006):

$$CO_2 + C \rightleftarrows 2CO \qquad (23)$$

On the other hand, when analyzed the effect of the fuel moisture was observed that the CO yield go down at higher water presence. This is supported by the behavior of the water-gas shift reaction, which promotes the CO consumption with water vapor according the Eq. (24):

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (24)$$

Figures 2 and 3 show, respectively, the H_2 and CH_4 yields obtained in function of the analyzed parameters.
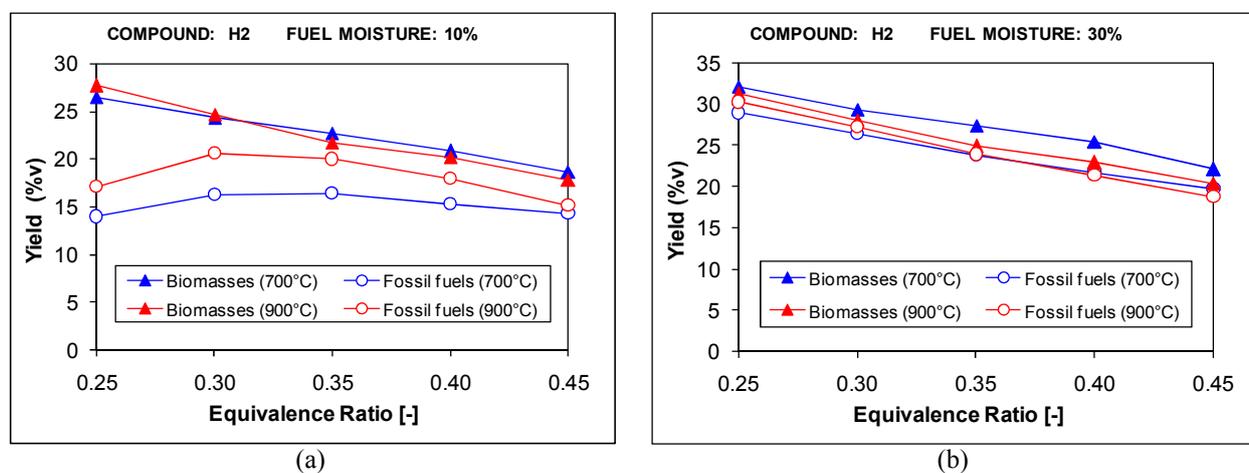
Figure 2. Volumetric yield of H_2 in flue gas (dry basis) in function of equivalence ratio and temperature reaction for 10% (a) and 30% (b) of fuel moisture.
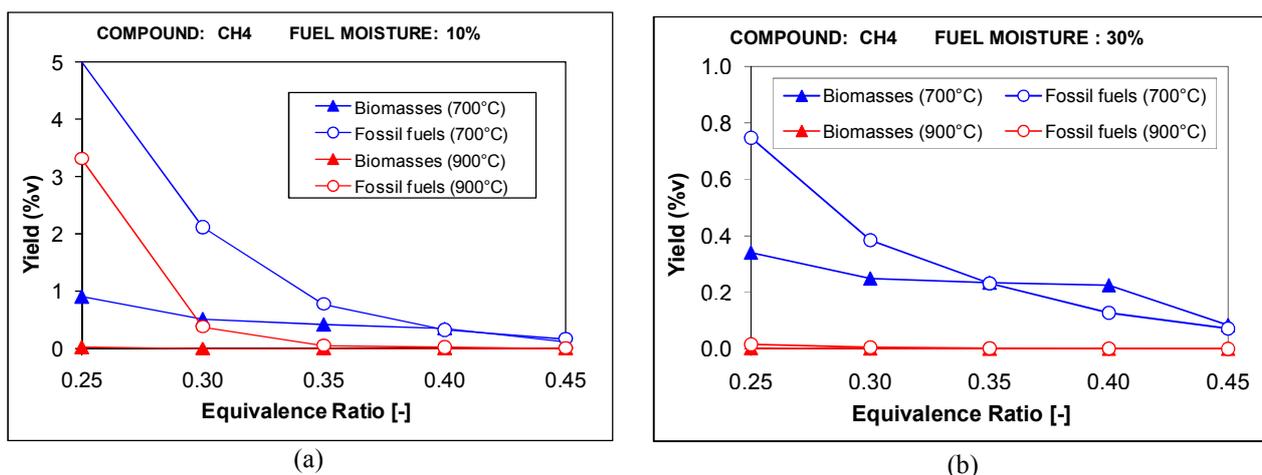
Figure 3. Volumetric yield of CH_4 in flue gas (dry basis) in function of equivalence ratio and temperature reaction for 10% (a) and 30% (b) of fuel moisture.

The results shown in Fig. 2 and Fig. 3 indicate that both H_2 and CH_4 follow the same tendency of the CO with the variation in equivalence ratio. This behavior is also explained by the higher conversion chances of the H_2 and CH_4 to H_2O and CO_2 through oxidation reactions.

The gas-water shift reaction explains the curves of the H_2 yields, which are in accordance with those obtained for the CO volumetric concentrations. So, higher fuel moistures clearly increase the H_2 presence in flue gas and reduce the CO concentration. On the other hand, at atmospheric pressure, low CH_4 yields in flue gas were obtained in most of simulations, as also found by Li *et al.* (2001) and Pellegrini and Oliveira (2007).

In general, fossil fuels had higher CO and CH_4 yields when compared with those attained for the biomasses. However, biomasses showed more elevated H_2 concentration in flue gas than fossil fuels. This can be explained by the differences in the ultimate analysis among fuels considering that the fossil fuels here studied have proportionally more carbon in dry and ash free basis that the biomasses.

Table 2 shows the HHV of the flue gas obtained from simulations of the biomasses and fossil fuels gasification. The HHVs were calculated according Eq. (22).

Table 2. High heating value of the flue gas obtained from simulations (MJ/Nm^3, dry basis)
Mean values in the equivalence ratio range analyzed.

Fuel/ Reaction temperature	Fuel moisture (% mass)	
	10%	30%
Biomasses/700°C	5.83	5.64
Biomasses/900°C	6.08	5.82
Fossil fuels/700°C	6.16	5.67
Fossil fuels/900°C	6.49	6.02

Results from Tab. 2 indicate that, for the ranges of the factors analyzed, the mean HHV of the flue gas produced from biomass is slightly lower than that found for fossil fuels (around 5.8 MJ/Nm^3 for biomass versus approximately 6.1 MJ/Nm^3 for fossil fuels). Further, was verified that the HHV of the flue gas increases with the reaction temperature and decrease with the fuel moisture because a minor CO presence is no balanced with a higher H_2 volumetric yield (Jarungthammachote and Dutta, 2007). In general, the HHV values obtained are in agreement with data available from literature (Schuster *et al.*, 2001; Sánchez, *et al.*, 2010).

The HHV profile in function of the equivalence ratio at 10% of fuel moisture is illustrated in Fig. 4, for the temperatures of 700 and 900°C.
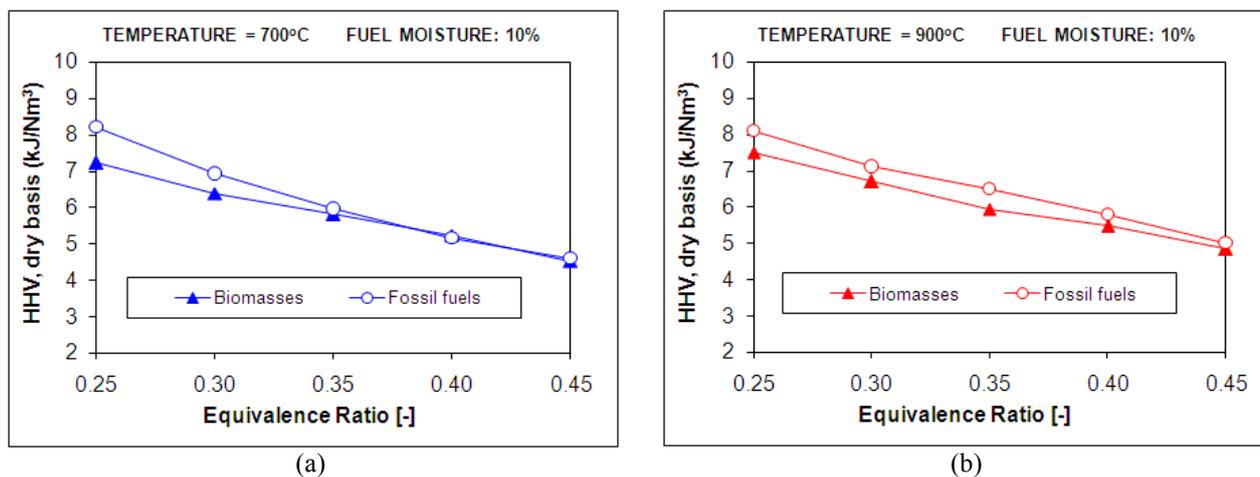
Figure 4. HHV profiles of the flue gas obtained from biomasses and fossil fuels in function of equivalence ratio at 10% of fuel moisture for temperature reactions of 700°C (a) and 900°C (b).

According to Fig. 4, the HHV of the flue gas tends to decrease with the equivalence ratio for both temperatures. As described before, this occurs because the oxidation reactions of energetic components (CO, H_2 and CH_4) become important when more air is used in the gasification process. Also, some tendency of separation between HHV profiles for biomass and fossil fuels was found at lower equivalence ratio values, which suggests that the difference in carbon/hydrogen relations from a fuel type to another is more relevant at lower oxygen participation.

5. CONCLUSIONS

In this work was verified that both the volumetric yield and the high heating value of producer gas originated from gasification reactions of several biomass and fossil fuels can be easily obtained through a computational algorithm

simulating the chemical equilibrium phenomenon. The quality of the producer gas generated from the solid fuels analyzed was in accordance with that indicated in previous researches, especially when the profiles of the energetic components (CO, H_2 and CH_4) in function of temperature reaction, fuel moisture and equivalence ratio were compared. Results suggest that the non-stoichiometric model based on the Gibbs free energy minimization approach can be an useful tool for preliminary design of gasifiers, as well as for prediction of the flue gas composition and energetic potential of solid fossil fuels and biomasses.

6. ACKNOWLEDGEMENTS

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